Proceedings of the
Eighth Cellulose Conference.
I. Wood Chemicals—
A Future Challenge

Editor:

T. E. Timell

19960314 012

APPLIED POLYMER SYMPOSIA NO. 28

Proceedings of the Eighth Cellulose Conference
I. Wood Chemicals—
A Future Challenge

Held at Syracuse, New York, May 19–23, 1975

Sponsored by
The Cellulose Research Institute, State University of New York College of Environmental Science and Forestry, and The Wood Chemistry Committee, Technical Association of the Pulp and Paper Industry

Editor
T. E. Timell
*SUNY College of Environmental Science and Forestry,
Syracuse, New York 13210*

an Interscience® Publication

Dedication

Herman F. Mark

To Whom the Proceedings of the
Eighth Cellulose Conference are Dedicated

With pride and pleasure we dedicate these Proceedings of the Eighth Cellulose Conference to Professor Herman F. Mark, one of the few "greats" of modern polymer chemistry. His name is so intertwined with the term polymer chemistry that they are practically synonymous throughout the world. He has served well the cause of chemistry at universities, research institutes, and industry in Austria, Germany, Canada, and the USA. Dr. Mark has received many of chemistry's highest awards, including several honorary degrees, in many countries. He is highly sought after as a plenary lecturer. Just this year he was invited to lecture in The Peoples' Republic of China.

Early in his career, Dr. Mark developed an interest in cellulose chemistry, and he made basic contributions to our knowledge of the crystal structure of cellulose, the nature of the cellulose molecule, and its orderly arrangement in nature. His work with cellulose and fibers brought him to the paper industry in Canada. His broad interest in cellulose and industrial wood chemistry led to his appointment as Chairman of the Wood Chemistry Committee of the Food and Agriculture Organization of The United Nations, a responsibility he held for many years.

Professor Mark was born in Vienna in 1895 and received his Ph.D. degree from The University of Vienna in 1921. His youth was shaped by his Viennese upbringing; he has long been an American citizen; but he really belongs to the world. He possesses marvelous human attributes; a genial, friendly personality, and the exceptional ability to generate interest and understanding in any assembly of persons regardless of the difficulty of the subject. In other words, he is an exceptional teacher.

The combination of Dr. Mark's acute scientific mind and warm human approach is the basis for his great capacity for organizing and developing programs. Likewise, it has made him universally welcome and in demand by the world's academic, industrial research, and other scientific circles.

EDWIN C. JAHN

Preface

The 106 papers collected in three volumes were presented at the Eighth Cellulose Conference, held in Syracuse, New York, on May 19-23, 1975, a meeting sponsored by the Cellulose Research Institute of the State University College of Environmental Science and Forestry. The conference, which attracted 420 participants, was centered around the use of wood and wood related materials as a future source of energy and chemicals. First planned in the summer of 1973, it received an added impetus as a result of the energy crisis in the fall of that year.

The papers presented can be divided into four different groups. The first symposium, "Wood Chemicals—A Future Challenge" was organized jointly with the Technical Association of the Pulp and Paper Industry, and was concerned with possibilities of better utilizing our forest resources, especially wood, as a source of energy and as a raw material for chemicals in the face of our dwindling supplies of fossil fuels, particularly petroleum. The second, closely related symposium on "Complete-Tree Utilization" was an attempt to summarize the present stand with respect to a more complete recovery of our forest trees.

The third symposium, entitled "Biosynthesis and Supermolecular Structure of Cellulose" dealt with recent advances in an important area, where much still remains to be elucidated. As has been the case with all previous cellulose conferences, a large number of unsolicited papers were also presented, most of them dealing with the chemistry of cellulose, hemicelluloses, lignin, and wood extractives or with the structure of wood and bark. In addition to the papers, the conference included a panel discussion, organized by Dr. S. I. Falkehag on the subject "Research and Educational Challenges Related to Wood Chemistry" with Dr. A. H. Nissan as Chairman and with participants representing government, industry, and universities. Dr. M. Kent Wilson spoke at the conference banquet on the topic: "Basic Research and the Energy Problem."

The present volume, which is the first in a series of three, contains 33 of the 39 papers presented at the symposium "Wood Chemicals—A Future Challenge." Included here are contributions discussing wood and bark as a source of energy and chemicals, future demand for and supply of wood, pyrolysis of wood, fermentation of cellulose, and improved utilization of lignin and recovery of silvichemicals. I wish to express my appreciation to all who took part in this symposium: the speakers, the presiding officers, the members of the panel, and all those who contributed to the discussions.

In the planning and organization of the Eighth Cellulose Conference, I received invaluable assistance from many persons, especially my colleagues Carlton W. Dence and Edwin C. Jahn, and Ingemar S. Falkehag, of the Westvaco Corporation. David S. Goheen, Crown Zellerbach Corporation, and Kyösti V. Sarkanen,

University of Washington, were also of much help.   I am grateful to Dr. E.E.
Palmer, President of this College, for his many efforts on behalf of the conference.
Austin Hamer and his staff must be given credit for the organization and smooth
operation of the conference.   Their great experience and dedication were invalu-
able.   Program, abstracts, and information material were ably handled by Ronald
Karns, John Novado, and their staff.   I also wish to express my gratitude to Mrs.
Theresa Scirocco, who handled the enormous correspondence associated with an
international meeting of this size.

We are all indebted to our publisher, Wiley-Interscience and to our production
manager, Mrs. Jeanne Rich.   Finally, I wish to express my appreciation to Profes-
sor Herman F. Mark, who as Editor has been instrumental in the publication of
these as well as earlier proceedings of our cellulose conferences.   In recognition of
his many contributions to cellulose chemistry, the Proceedings of the Eighth Cellu-
lose Conference are dedicated to him.

<div align="right">T. E. TIMELL</div>

SUNY College of Environmental
Science and Forestry
Syracuse, New York 13210

Contents

BIOMASS ENERGY REFINERIES FOR PRODUCTION OF FUEL AND FERTILIZER

THOMAS B. REED

*Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

SYNOPSIS

As we approach the limits of growth of man on Planet Earth we face shortages of energy, materials, and clean air and water. We can extend these three limits simultaneously by closing the recycle loops between man's disposal sites for solid waste and sewage, and manufacture and agriculture where we now consume fresh supplies of energy and materials. The development of "biomass energy refineries" will be required to close these loops.

Presently collected or collectible biomass in the U. S. has an energy content of about 8×10^{15} million Btu, or about 10% of total energy consumption. At a solar conversion efficiency of 1/2% our farms and forests could harvest 69×10^{15} million Btu, about equal to our present energy consumption, while simultaneously satisfying all of our needs for food and fiber. We are fortunate that processes already exist which can convert wet and dry biomass into more usable fuel forms. Anaerobic digestion or fermentation can convert dilute biomass to methane or alcohols. Thermal processes can make charcoal, oils, fuel gases, or methanol from dry biomass.

Partial combustion of waste biomass with oxygen to make synthesis gas ($CO + H_2$) is particularly attractive and a 200 ton/day plant has recently been tested for municipal wastes. An energy and mass balance for conversion of municipal waste is presented along with the costs for converting coal, waste, and wood to methanol. The City of Seattle has recently issued a request for proposal for the construction of a plant to convert 1500 tons/day of municipal waste into methanol or ammonia.

INTRODUCTION

Since man has become civilized he has used food, materials, and energy in an open cycle system represented by the solid lines of Figure 1. We produce food and some of our raw materials in agriculture and silviculture. The balance of our raw materials and most of our energy comes from mining and drilling. Having used these materials, we then discharge the remains to dumps and sewers, the bowels and kidneys of our cities, where they have accumulated, causing severe constipation; the fuel emissions poison our air and water.

Rising population and, more importantly, rising consumption have now tested the "Limits of Growth" that can be sustained by our country and our planet and fewer of us will have to consume less if man is to remain on this planet. More at-

1
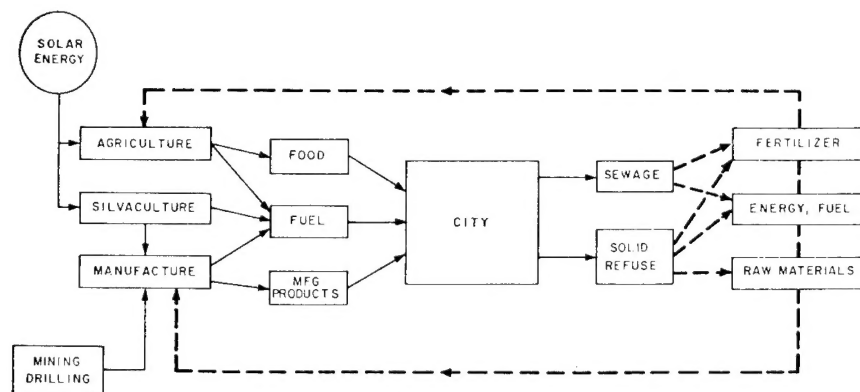
·FIG. 1. Material and energy flow in the recycling society.

tractive than reducing our legitimate needs, however, would be reducing our waste and consumption of nonrenewable resources by closing the recycle loops (dotted) of Figure 1, and establishing new energy sources and material.

We have already begun some material recovery with limited paper and metal recycling at a few municipal dumps. Some energy is being recycled in solid form for power or steam generation. This paper will discuss available methods for possible conversion of waste or harvested biomass to fuels, and outlines costs for a waste and wood "energy refinery."

BIOMASS PRODUCTION

Nature converts solar energy to biomass in all its infinite varieties with an efficiency of 0.1–2%. The energy content of dry biomass is remarkably constant, averaging about 16 million Btu/ton. The chemical composition varies somewhat more with species, and approximates $C_3H_4O_2$ for wood. The sulfur content of biomass is generally below 0.1% (coal is typically 2%) and the ash is typically 2% and can be used as fertilizer.

The total biomass production of the world has been estimated [1] as 146×10^9 tons, with an energy content of 2300×10^{15} Btu or about 30 times the U. S. consumption of 70×10^{15} Btu/yr. At a solar conversion efficiency of $\frac{1}{2}$%, the 520×10^6 acres of commercial forests in the U. S. (23% of 48 state area) and the 340×10^6 acres of farmland (15% of 48 state area) would produce 4.3×10^9 tons of dry biomass with an energy content of 69×10^{15} Btu, about equal to the total present U. S. energy consumption [2].

One estimate of collected or collectible waste biomass is shown in Table I [3]. The total U. S. biomass production shown in Table I is 588×10^6 dry tons/yr; others estimate 650 and 136×10^6 dry tons/yr [4,5]. The assumptions used in deriving such figures vary so greatly that they should only convey the idea that waste biomass could provide a significant fraction of our energy needs. Until the collection and conversion processes are specified and developed, we cannot determine total waste biomass available more accurately. 500×10^6 dry tons/yr would have an energy content of 8×10^{15} Btu/yr, about 10% of our present energy consumption in the U. S.

TABLE I
Waste Biomass Collected or Collectible Annually in the U.S.

SOURCE	MM dry tons/yr.
Municipal waste	170
Sewage	60
Forest Industries	120
Field Crops & Processing Residues	64
Manure	174
Total Wet Biomass (Dry basis)	234
Total Dry Biomass	354
Total Biomass	588[a]

[a] Total energy content = 8.2×10^{15} Btu, 12% of U.S. Energy Consumption (assuming 9 million Btu/ton for municipal waste and 16 million Btu/ton for dry biomass).

In addition to waste biomass, we have the potential to grow a great deal more biomass, either in conjunction with food or fiber production, or in energy farms devoted exclusively to biomass production. It is estimated that biomass can be produced for energy at costs of between $7 and $20/ton, including all capital, land, energy, and chemical costs [4,5]. (Biomass at $16/ton is equivalent to an energy cost of $1/million Btu—present gas prices are around $2/million Btu).

In Maine, ½ to 1 ton of pulp or lumber/acre are harvested on a continuous basis. However, anywhere from 2 to 4 tons/acre are left behind in the form of puckerbrush (nonmercantable trees) plus brush and slash [6]. During the past decade large machines have been developed capable of harvesting and chipping the "whole tree" in the forest. In assessing the potential of wood for supplying energy, we need to determine the "incremental cost" of fuel wood. This is the cost of low grade chips from bark, leaves, and branches collected while harvesting prime white chips for paper or prime wood for lumber. If wood is harvested as an energy source, its economic value will permit a better use of the "whole tree" and the "whole forest." A well managed forest will have much higher yields and will be a better forest for plants, animals, and humans.

In short, biomass is an environmentally attractive, renewable energy source, provided we can economically convert it to useful fuel forms.

WET BIOMASS CONVERSION PROCESSES

It is impractical to use biomass for heating our homes or running our cars unless we convert it to other forms, more conveniently shipped, stored, and used, with the biological or thermal conversion processes outlined in Figure 2. The wet biomass conversion routes shown parallel those used by nature in building our enormous fossil fuel reserves from a miniscule fraction of the biomass produced during the coal age, or conversion of the remaining biomass back to CO_2 and water for steady state recycle over the past billion years. These processes proceed relatively slowly near room temperature in the presence of water or air, and are most appropriate when the biomass is dilute and in a form (such as sewage) readily attacked by microorganisms.

Bioconversion processes require well controlled temperatures and proper concentrations of oxygen and nutrients to work well. For each ton of fuel produced,
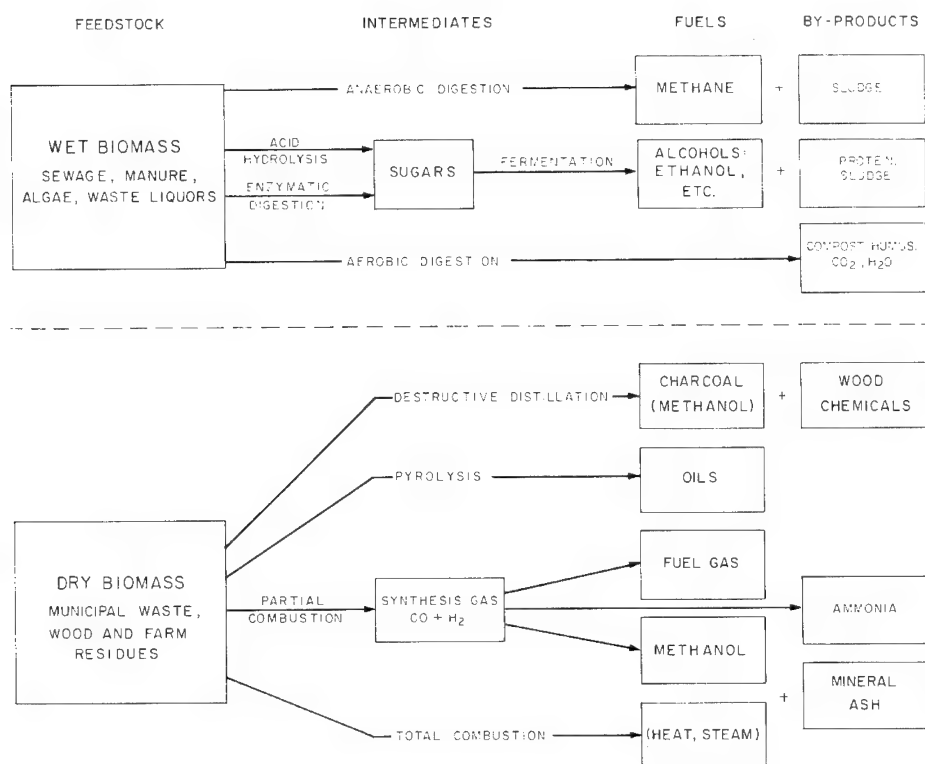
FIG. 2. Biomass to fuel conversion routes.

there will be ten or more tons of water to be processed and disposed of. Bioconversion processes ultimately leave a "sludge" of organic and inorganic material which cannot be further digested by microorganisms. These sludges have some potential for use as fertilizer, but where necessary they can be burned in thermal processes along with dry biomass. Heat can convert what microorganisms won't attack.

Studies are underway on the conversion of wet biomass to methane and ethanol for fuel. A great deal of ethanol was produced in Europe from wood and farm products between 1930 and 1945 for blending with gasoline as a fuel. In 1935 four million cars in 11 countries consumed 576,000 tons of methanol and ethanol for this purpose [7]. Conversion of biomass to ethanol is a two stage process. If the biomass is relatively pure cellulose, such as paper, an enzyme, *Trichorderma viride,* now being investigated at the Army Natick laboratories, will hydrolyze the cellulose to sugars [8]. Alternatively, acid hydrolysis has long been used to break down wood to sugar, and ethanol is being made from the wood sugars that occur naturally while making paper. Other sources of alcohol and protein are the distiller's dried grains remaining after manufacture of beverage alcohol [9]. The sugars so formed are then fermented to 12% alcohol by the process of fermentation perfected in Babylonia in 6000 BC. The alcohol is distilled, a process developed in 1100 AD in Spain and Holland. A fleet test of 35 Nebraska State cars and trucks is now being performed using 10% ethanol in gasoline at the University of Nebraska [10].

Methane (sewer gas, natural gas, marsh gas, mine gas, etc.) is produced by the anaerobic digestion of biomass by *Escherichia coli.* Sewer gas is often used to drive power equipment in sewage plants and has been used for city gas in Birmingham, England. Large quantities of manure are presently generated in cattle feed lots, and an experiment is under way to convert this to pipeline gas. It has been suggested that we could establish a "perpetual methane economy" using methane produced by digestion [5,11]. Cellulose and wood are not attacked by *E. coli,* because they contain very little nitrogen, but when added to sewage and manure, the yields of methane are greatly increased [12].

DRY BIOMASS CONVERSION PROCESSES

Nature has designed some biomass, such as wood, to be highly resistant to biological attack so that a great deal of energy must be expended (pulping, grinding, etc.) to make these forms susceptible to bioconversion. In these cases, thermal conversion using fire or heat offers high reaction rates in relatively small plants and can convert a wide variety of feedstocks to a single product or a variety of products. Simple combustion was of course used by man to convert wood to useful heat before recorded history began. For indoor heating, and later for metallurgical purposes, charcoal was made in enormous quantities by the destructive distillation of wood; in the last century the vapors from wood distillation were condensed to produce methanol, acetic acid, and wood chemicals for an early "silvichemical" industry. The last such plant closed about 1960.

In an effort to generate useful energy forms while disposing of municipal waste, a number of pyrolysis processes have been developed. The Monsanto process produces char and pyrolysis gases from solid waste and fuel oil. The Pyrotek process produces combustible gases by heating shredded solid waste. The Garrett Pyrolysis process uses flash pyrolysis to produce a high viscosity oxygenated fuel oil from waste [13].

As shown in Figure 2, partial combustion with air or oxygen of biomass to synthesis gas offers a route to either low or medium fuel gas respectively. This gas can be burned for heat, or can be converted catalytically to methanol, methane, or ammonia. Depending on the gasification method used, part of the biomass can also be obtained in the form of an oil and associated wood chemicals (Lurgi and Purox processes) or all the biomass can be converted to gas. An important consideration necessary for evaluating the processes of Figure 2 is a complete mass and energy balance for the process, and for most of the processes of Figure 2 these data are not available.

METHANOL—A CLEAN FUEL FROM BIOMASS

Methanol is a clean, easily stored liquid fuel which can be burned in internal combustion engines, turbines, and fuel cells to help supply our energy needs [14–17]. This useful chemical is now primarily manufactured from natural gas. About a billion gallons of methanol are presently made in the U. S. each year and are used mostly for plastic manufacture. There are a number of processes which can be used potentially to convert biomass to synthesis gas, but only the PUROX
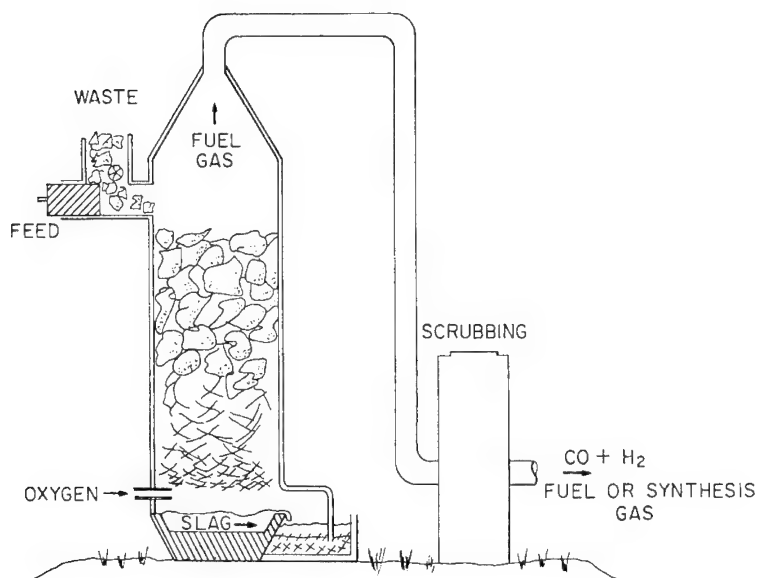
FIG. 3. Oxygen waste disposal furnace.

process [18–20] developed by Union Carbide for municipal waste disposal has been studied in sufficient detail to permit energy balance and cost analysis; if biomass becomes a primary energy source, others will be developed.

BIOMASS GASIFICATION

The Purox gasifier consists of a shaft furnace 15 ft in diam and 45 ft high as shown in Figure 3. Waste, shredded to about 4 in. diam, and separated if desired, is fed into the top of the furnace through a ram-seal. Oxygen is fed to the bottom of the furnace and burns the char at about 1500°C to form carbon monoxide which rises through the mass, exchanging heat and pyrolyzing the incoming waste. The metals and glasses present melt to form an inert slag representing 2% of the volume of the original waste. The remainder of the waste is converted to a gas plus a small amount of oxygenated oil which can be stored or reburned to gas.

TABLE II

Mass and Energy Balance for Production of Fuel Gas or Methanol from Solid Waste[a]

	Waste		Synthesis gas	Methanol
	Waste +	Oxygen		
		O_2	$CO + H_2$	CH_3OH
Mass - tons	1.0	0.2	1.0	0.2 [b]
Energy content-MMBTU	9	0.2 [c]	7	4

[a] Based on results in U. S. Patent 3,729,298.

[b] Assuming 40% energy conversion efficiency.

[c] Based on a consumption of 240 kW hr/ton O_2 produced.

The mass and energy balances for this process are shown in Table II. The gas, after cleaning, is composed (by volume) of 47% CO; 33% H_2; 5% CH_4; 1% N_2; and 14% CO_2.

ECONOMICS OF METHANOL PRODUCTION FROM COAL, WASTE, AND WOOD

Table III examines the economics of conversion of coal, waste, and wood to methanol through combustion to synthesis gas. The costs for conversion of coal are taken from a recent Atomic Energy Commission study [3]. The costs for conversion of waste are taken in part from studies by the City of Seattle and Mathematical Sciences Northwest, Inc., based on the use of the Purox gasifier [13,21]. The cost in Table III assumes a methyl-fuel plant cost of 8 million dollars rather than the 21 million assumed in that study. It is assumed here that five tons of waste are required to produce one ton of methanol, based on conversion of 40% of the energy in the waste to methanol. The City of Seattle has recently issued a Request for Proposal [22] on a 1500 ton/day waste plant projected to cost $56 million. An artist's sketch of the plant is shown in Figure 4.

It is more difficult to estimate the cost of production of methanol from biomass and wood, since no gasifiers presently exist designed for this purpose. Because of the higher energy density of wood, we assumed that three gasifiers such as the Purox unit could convert 900 tons/day into 300 tons/day of methanol (40% energy conversion). It is assumed that the wood costs $5/ton.

The present cost of methanol is $0.38/gal, and the figures in Table III would suggest that methanol could be made economically from any of these primary en-

TABLE III
Cost of Methanol Production from Coal, Waste, and Wood

RAW MATERIALS		WASTE[a]	WOOD[b]	COAL[c]
Fuel consumed	tons/day	1500	900	11,690
Methanol produced	tons/day	300	300	5,000
CAPITAL COSTS (MILLIONS)				
Gasification & oxygen plant		19.8	11.8	83.4
Methanol plant		8.1	8.1	66.7
Total Plant		27.9	19.9	150.1
Offsites, contingencies & construction		16.0	9.6	90.2
Total capital		43.9	29.5	240.9
ANNUAL COSTS (Millions)				
Debt		5.1	4.0	29.2
Operating cost		5.5	3.3	35.9
Fuel		-5.5	1.6	14.7
METHANOL COST (¢/gal)				
Production		29.0	20.0	10.9
Fuel		-15.2	4.5	2.5
Total		13.8	24.5	13.5

[a] Assuming 15 year plant life, 8% debt financing, fuel credit of $10/ton for municipal waste. (Figures in part from Seattle study).

[b] Assuming 15 year plant life, 10.5% utility debt financing, $5/ton of wood.

[c] Assuming 20 year plant life, 10.5% utility financing, $3.46/ton for Western subbituminous coal. (Coal figures abstracted from AEC study [3].)
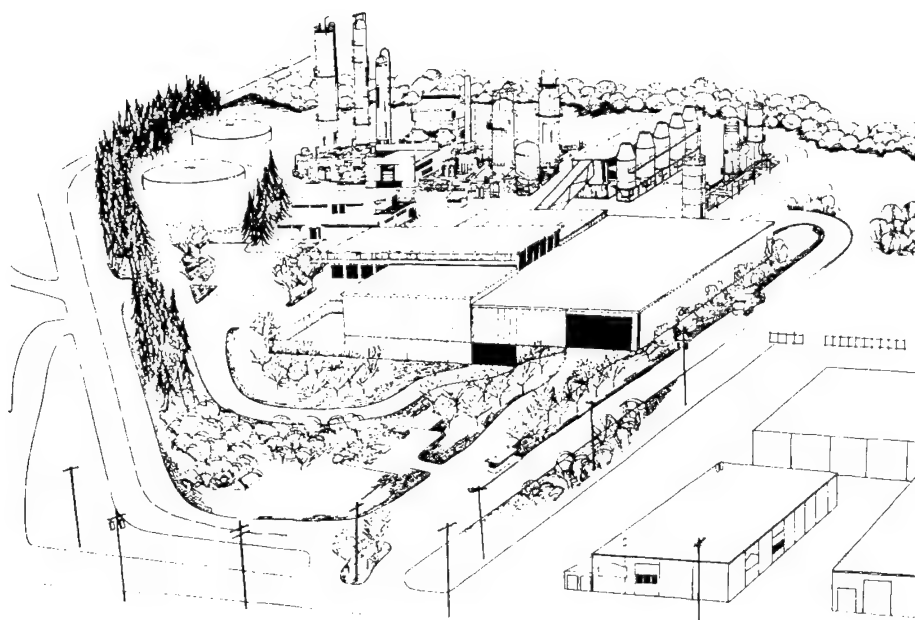
FIG. 4. Seattle solid waste/methanol/ammonia project.

ergy sources. However, the manufacture of methanol and other synthetic fuels is highly capital intensive, and the cost of the methanol produced in the relatively small scale wood plant considered here is probably not low enough to attract private capital. The costs shown might be decreased considerably by development of gasifiers specifically designed for wood and improvements in wood harvesting and transport technology. Continually rising prices for other energy forms will make these prices more attractive. Although no commercial processes have been developed at present for the gasification or liquifaction of wood or farm residues, presumably much of the technology developed for coal gasification can also be applied to processing biomass.

CONCLUSION

Biomass is an abundant, clean, and in some forms economically attractive primary source of energy and especially fuel, which could help to replace our diminishing fuel supplies. Many processes exist in various stages of development for conversion of wet or dry biomass to liquid or gaseous fuels and chemicals.

The energy content of U. S. municipal, farm, and forest wastes is about 10% of the U. S. total energy consumption. Efficient use of our present farms and forest could produce biomass energy equal to our total consumption along with food and fiber production.

Municipal waste may be the most economical biomass source for production of methanol or ammonia and a cost of 13.8¢/gal is projected for manufacture of 300 tons/day of methanol from 1500 tons/day of municipal waste. The City of Seattle has issued a request for proposal on such a plant expected to cost $56 million. Commercial processes have not yet been developed for gasification or liquifaction

of wood or farm residues, but presumably much of the technology developed for coal gasification can also be applied to processing biomass.

REFERENCES

[1] G. A. Riley, *Am. Scientist, 32,* 129 (1964).

[2] T. Reed and R. M. Lerner, *Science, 182,* 1299 (1973).

[3] H. Jaffe et al. "Methanol from Coal for the Automotive Market," AEC Report (WASH No. 1337-2), Washington, D.C., Feb 1974.

[4] J. A. Alich and R. E. Inman, "Effective Utilization of Solar Energy to Produce Clean Fuel," Stanford Research Institute, Project 2643, (NSF/RANN/SE/GI 38723/FR/74/2).

[5] D. L. Klass, "A Long-range Approach to the Natural Gas Shortage Utilizing Nonfossil Renewable Carbon," from Symposium on Unusual Fuels Production; Vol. 20, No. 2. American Chemical Society, Philadelphia, Pa. April 6-11, 1975, p. 33.

[6] H. Young, "Biomass Variation in Puckerbrush Stands," in IUFRU Biomass Studies, Information at Union of Forest Research Organizations, August, 1973, p. 195.

[7] A. W. Nash and D. A. Howes, *Principles of Motor Fuel Preparation and Application,* Vol. I, Wiley, New York, 1938, pp. 461-561.

[8] M. Mandels, L. Hontz, and D. Brandt, "Disposal of Cellulosic Waste Materials by Enzymatic Hydrolysis," Army Science Conference Proceedings, Vol. 3, June 1972 AD 750 351:16-31. Also U. S. Patent 3,764,475, Oct. 9, 1973.

[9] W. A. Scheller and B. J. Mohr, "Production of Ethanol and Vegetable Protein by Grain Fermentation," from Symposium on Unusual Fuel Chemistry, American Chemical Society, Philadelphia, Pa., April 6-11, 1975, p. 54.

[10] W. A. Scheller and B. J. Mohr, "Performance of an Ethanol-Gasoline Blend in Automobiles and Light Trucks," *ibid,* p. 71.

[11] D. L. Klass, *Chem. Technol., 4,* 161 (1974).

[12] G. E. Johnson, patent specification MIN 1624.

[13] R. G. Sheehan et al, "Seattle's Solid Waste . . . An Untapped Resource," study prepared by P. A. Wiatrek, G. Vickery et al of the Seattle Engineering Department and Seattle Department of Lighting.

[14] T. B. Reed, R. M. Lerner, E. D. Hinkley, and R. E. Fahey, "Improved Performance of Internal Combustion Engines using 5-30% methanol in Gasoline," Paper No. 749104 in Intersociety Energy Conversion Engineering Conference, San Francisco, CA, Aug 1974.

[15] T. B. Reed and R. M. Lerner, "Sources and Methods of Methanol Production," in proceedings, THEME Conference, Miami Beach, March 18, 1974.

[16] H. Heitland, W. Bernhardt, and W. Lee, "Comparative Investigation of Methanol and Gasoline Performance in Motor Vehicles," Paper at NATO CCMS Symposium, Dusseldorf, Nov 1974.

[17] G. A. Mills and B. M. Harney, "Methanol-The 'New Fuel' from Coal," Chemtech, Jan 1974, p. 26.

[18] J. E. Anderson, U. S. Patent 3,729,298 (1973).

[19] H. W. Schulz, "Design of an Integrated Waste Management System for the City of New York: Findings and Recommendations," June 21, 1974. (Interim report prepared under NSF project.)

[20] *Chem. Engineering News,* Nov. 25, 1974, p. 83.

[21] "Feasibility Study: Conversion of Solid Waste to Methanol or Ammonia," prepared for the City of Seattle by Mathematical Sciences Northwest, Inc., Sept. 6, 1974.

[22] "Methanol or Ammonia from Municipal Solid Waste," a Request for Proposals by City of Seattle.

THE ENERGY PLANTATION

CLINTON C. KEMP, GEORGE C. SZEGO, and MALCOLM D. FRASER

InterTechnology Corporation, Warrenton
Virginia 22186

Fossil fuels have three outstanding virtues. They are a natural storage system from which energy can be recovered almost anywhere at any time, at will. Their energy can be released at high temperature which means that it has a high capacity for producing work, or as the thermodynamicists say, it has high thermodynamic availability. Their energy is stored at high density, characteristically between about 10,000 and 24,000 Btu/lb.

Fossil fuels have two insurmountable drawbacks. As is well-known, the supply of many of their more desirable embodiments is approaching exhaustion, and is creating near-term difficulties for this nation. The second drawback is the environmental problems associated with their continued and increasing use. These problems are not for certain limited to sulfur and nitrogen oxides, particulates, and trace contaminants. They may also involve noticeable interference with the carbon dioxide and thermal balances of the earth within the next few decades.

Fissionable nuclear fuels have attractive features approximately comparable with the three major virtues of fossil fuel. They also have at least two possibly serious drawbacks. One of these is that their supply from relatively inexpensive sources is being rapidly exhausted—a state of affairs which cannot be stemmed unless and until breeder reactors gain general public acceptance and are in widespread operation. The other is the plethora of actual and conjectured hazards their production and use bring for man and his delicately balanced environment on this earth. Being able to surmount these substantial hurdles is not a clear certainty at this time.

Prudence therefore dictates that we continue to seek and perfect, if only to hedge our energy supply bets, at least one large-scale nonfossil—nonnuclear energy source which will be:

capable of storing energy for our use at will,
high in thermodynamic availability,
forever renewable,
ecologically inoffensive,
widely available in the United States,

11

TABLE I

Conceivable Nonfossil, Nonnuclear Means for Meeting Energy Requirements on a Large Scale
in the Near Future

Conceivable Means	A Major Practical Hurdle
Non solar:	
geothermal	not widely available
tides	few satisfactory sites
municipal garbage	limited supply
agricultural refuse	limited supply
feed lot refuse	limited supply
Indirectly Solar:	
winds	energy storage
ocean thermal gradients	construction materials
Directly Solar:	
low temperature photothermal	initial cost
high temperature photothermal	initial cost and energy storage
photovoltaic	initial cost and energy storage
photosynthesis	credibility

dependent on technology already available,
operable on a large scale within a decade or two,
developable within our manpower and material resources,
tolerably priced, and
free of hazard potentials.

The recognized nonfossil—nonnuclear energy source possibilities fall into three groups, differentiated from one another by the immediacy of their dependence on solar radiation. It will be seen from Table I that those in the nonsolar group generally have a practical energy-providing capacity which is small compared with our national needs (two to three per cent of the total U.S. consumption in 1972). Energy storage is an unsolved problem for at least three of the possibilities which depend directly or indirectly on solar radiation. Only energy sources based on ocean thermal gradients and on photosynthesis are forever renewable, and also have naturally provided built-in solar energy storage capability, the potential for releasing energy with high thermodynamic availability, and capacity for meeting a large part of our future energy requirements without serious ecological detraction.

Little attention has been given until recently to the possibility of capturing solar radiation in land plants grown purposely for their fuel value, in that we call Energy Plantations. It is worth considering this possibility seriously because plants, as they grow, serve as convenient single-service disposable solar energy storage devices from which the accumulated energy can be released, at will, at temperatures comparable with those achievable from fossil fuels. Incidentally, plant matter is not an inconsequential source of energy these days because, even as recently as last year, more energy was derived from materials of forest origin than from nuclear plants in the United States.

In the ensuing appraisal of the merit of harnessing solar radiation in Energy Plantations by photosynthesis on a scale adequate for meeting the needs of large

TABLE II

"Incidental" Fuel Value Yields from Selected Plants Grown in the United States [1] footnotes:

Plant and (Location)	Air-Dry Tons Per Acre-Year[a]	Useful Fuel Value 10^6 Btu Per Acre-Year[b]	Solar Energy Conversion Rate[c]
Reed Canary Grass (Midwest)	7	80	0.4%
Bermuda Grass (Alabama)	8 - 11	90 - 130	0.4 - 0.6%
Corn Silage (Midwest)	8 - 12	90 - 140	0.4 - 0.7%
Forage Sorghum (Kansas)	6 - 17	70 - 195	0.3 - 0.9%
Sugarcane (Florida and Louisiana)	17 - 22	195 - 260	0.9 - 1.2%
General Agriculture (United States)	3 - 16	35 - 185	0.2 - 0.9%
Hybrid Poplar (Pennsylvania)	4 - 8	45 - 120	0.2 - 0.6%
Sycamore (Georgia)	2 - 11	25 - 130	0.1 - 0.6%
Southern Pine (South)	2 - 5	28 - 70	0.1 - 0.3%

[a] About 12 lb water/100 lb of oven-dry weight.

[b] 5,800 Btu/lb air-dry weight is equivalent to the lower heating value (i.e., moisture in the products of combustion is not condensed to liquid water), except Southern pine for which 7,000 Btu/lb air-dry is used.

[c] Calculated by dividing the useful fuel value produced per acre-year by the total solar radiation incident on the growing site during an entire year.

energy consumers, such as electric utilities, attention will first be given to the annual fuel yield which can be expected per acre. Then the cost of the fuel so produced will be discussed, and it will be shown that certain plant species grown at selected planting densities and harvest schedules are preferred for Btu Bushes. Finally, land requirements and land availability for producing energy on a large scale in Energy Plantations will be reviewed. The appraisal will be limited to production of solid fuels, although it should be noted that the product of Energy Plantations can probably be converted at tolerable cost to fuel gas or synthetic natural gas by anaerobic biological digestion.

Plant material is not grown on a large scale purposely for its fuel value in any of the developed countries these days. Consequently, there are no data on expected fuel value yields. But the fuel values incidentally produced by plants grown for food, fodder, or fiber can be used as a basis for estimating such yields. Especially realistic estimates of the output from Energy Plantations will come from consideration of plants valued for substantially their entire structure above ground. A representative list of "incidental" fuel value yields from such plants is given in Table II. The solar energy conversion rates shown in this table are the fraction of the annual solar radiation incident on the land where the plants are grown which is stored as fuel value above ground by the plants. We have assumed an average annual solar radiation rate of 1,300 Btu/ft^2/day. This insolation rate is characteristic for about a third of the United States.

It is evident from the data in Table II, that without even trying to grow them for fuel, several plants grown in various parts of the country on a large scale by

TABLE III

Estimated Prices for Fuel Value Derived from Corn Grown for Silage at 1973 Costs for Field
Operations and June 1974 Costs for Fertilizer, Pesticide, and Seed

	Solar Energy Conversion Rate		
	0.4%/Year	0.7%/Year	1%/Year
Air-Dry Tons of Silage Per Acre Per Year	7.3	12.4	17.8
Fuel Value Produced-Btu Per Acre Per Year	85×10^6	145×10^6	207×10^6
Crop Raising Cost Per Acre	$ 99	$ 153	$ 209
General Expense	33	33	34
Land Profit	28	28	28
Total Cost	$ 160	$ 214	$ 271
Cost Per 10^6 Btu	$ 1.88	$ 1.48	$ 1.31

present crop production methods are collecting and storing fuel value in their substance above ground equivalent to between about 0.4 and about 0.7% of the annual solar radiation incident on the land on which they are grown. This sunshine conversion rate is equivalent to collecting and storing between about 80 and 140 million Btu/acre/year, or between about 13 and 23 barrels of crude oil/acre/year. It seems likely therefore that a solar energy conversion rate equivalent to about 0.6 or 0.7% can be achieved widely by optimizing plant-material production for fuel value by such means as: 1) double cropping where the growing season permits; 2) using planting densities and harvesting schedules which favor high plant-matter production rates; 3) selecting C_4 and other plant species which produce plant material at high rates; and 4) using mixed-species plantings, or crop rotations, which favor high plant-matter production rates.

The technology for taking all these steps is already well in hand and, in fact, in general use in various sectors of our agricultural, tree farming, and grassland range economies.

The cost of producing fuel in Energy Plantations depends on a number of factors, the fundamentally more influential of which are illustrated by three representative sets of cost estimates. The first of these is summarized in Table III. It is based on large-scale production of corn for silage in the Midwest. This estimate includes all sources of cost incurred directly and indirectly in producing chopped silage loaded in trucks ready for transport from the farm. It is assumed that field operations are performed by hired custom service operators at custom prices in effect in the Midwest in 1973 [2]. They therefore include operator profit. Prices in effect in June 1974 have been assumed for the cost of seed, fertilizer, and pesticides. The national average price of farmland sold in 1973 has been used as the base for calculating the 10% profit before income tax on the land used. The other assumptions used in making these estimates are to be found in reference [3].

It will be seen from Table III that at the reasonably attainable conversion of around 0.7% of the annual insolation falling on the corn field, the fuel value produced by the corn crop will cost about $1.50/million Btu at costs approximating
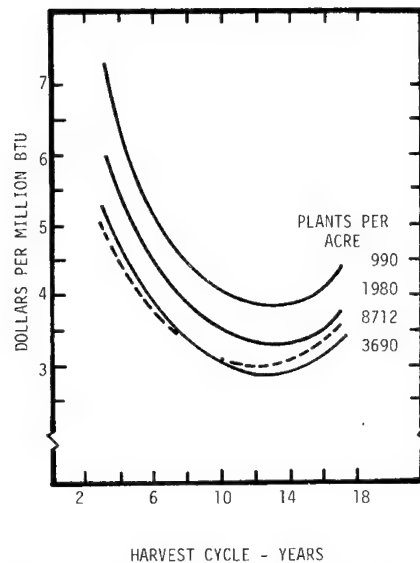
FIG. 1. Representative cost of fuel value from a Southern pine as a function of plants per acre.

those in effect at present. We believe this cost is more representative of the upper limit of the probable cost range for energy stored in annual plants grown under Energy Plantation conditions because: 1) the cost does not reflect the effects of optimizing operations for fuel value production; 2) field operations are assumed to be performed by hired custom operators, which is usually a relatively expensive way for doing the work, and therefore unlikely to be the practice in ongoing Energy Plantation operations; 3) sorghum, with its higher annual yield and hence lower fuel value cost, is likely to be preferred over corn; and 4) no allowance is made for the contribution to fertilizer cost which is likely to come from recycling the ash from the burned fuel to the Energy Plantation. After allowance for these various factors, the cost of fuel value produced by a preferred annual crop is likely to be between about $1.10 and $1.30/million Btu, at the current price level, in those parts of the country where rainfall is 20 in. or more a year, the land is flat to gently rolling, and the soil is a few feet deep.

This cost range is substantially lower than the current cost of hydrocarbon fuels used by the electric utilities in this country, and compares favorably with the cost of coal used by those in the District of Columbia and northeastern states other than Pennsylvania. According to data regularly compiled by the Federal Power Commission [4], the national average cost of fuel oils used by the electric utilities in April 1974 was $1.87/million Btu. The average cost of coal used in the northeastern states (except Pennsylvania) was $1.19/million Btu.

The second set of cost estimates (Fig. 1) assumes that a perennial, specifically a conifer, is the Btu Bush grown in the Energy Plantation. The conifer is a Southern pine having an intermediate resin content, and therefore a useful heating value of about 7,000 Btu/air-dry lb. Cost estimates are shown for planting densities ranging from about 1,000 to nearly 9,000 plants/acre, with harvest cycles from 3 to 17 years duration. The harvest yields under these various conditions are based on data from pines grown on the coastal plain in South Carolina [5]. The plant-

ing densities and harvest cycles are respectively higher and shorter than is conventional for pulpwood tree farming in the South, where usual practice, dictated by pulpwood specification, is about 800 trees/acre harvested on 20 to 30 year schedules. Since trees as large as those required for pulpwood are not needed for fuel production, higher planting densities are beneficial in an Energy Plantation because they enhance the rate/acre at which solar radiation is converted to stored fuel value by the Btu Bushes while they are young. However, at these higher planting densities, harvest cycles must be shortened to avoid impairment of the ultimate annual sustained fuel value yield because of interference, which develops increasingly between adjacent plants as they grow older.

The cost estimates shown in Figure 1 include all sources of cost incurred directly and indirectly in producing chipped fuel product loaded in trucks ready for transport from the harvesting area. Field operations are assumed to have been carried out by hired custom operators at costs in effect in 1973. June 1974 costs have been assumed for fertilizer and pesticides. It is assumed that the ash produced from the Energy Plantation fuel is recycled to the plantation where it serves to reduce the potash and phosphate fertilizer requirements. It is also assumed that all costs incurred for a particular crop planting are carried in an in-process inventory until the planting is harvested and sold some years later. The cost of capital required to finance these in-process inventories is assumed to be 10% per annum. The national average price of farmland in 1973 has been used as the base for calculating the 10% profit before income taxes on the land included in the estimates.

The estimates summarized in Figure 1 show that the cost of fuel value produced by conifers is markedly dependent on planting density and the length of the harvest cycle. At all planting densities, the cost of harvested useful fuel value stored by the Btu Bushes first declines and then increases fairly sharply as the harvest cycle is extended. The costs pass through minima at harvest cycles between about 11 and 13 years duration. The cost is also seen to pass through an absolute minimum at planting densities between 4,000 and about 9,000 plants/acre. Close analysis of the estimates summarized in Figure 1 suggests that at costs of production approximating those presently in effect, and at a 10% per annum cost of capital, the absolute minimum fuel value cost is reached at a planting density of about 6,000 plants per acre and a harvest cycle about 12 years long. Under these conditions, the estimated cost is moderately less than $3.00/million Btu of useful fuel value.

The cost of fuel value produced by conifers appears to be nearly three times that from annual crops such as corn or sorghum. There are a number of reasons for this difference. Conifers, at least when they are young, grow rather slowly and are therefore poor converters of solar energy into stored fuel value. The highest average annual solar energy conversion rate represented by the estimates in Figure 1 is only about 0.4% of the insolation incident on the plantation. This rate is at the lower end of the range achieved by corn and sorghum (see Table II). A second major contributor to the cost of fuel value from conifers, or any other perennial which takes many years to reach Calorie Crop maturity, is the cost of financing the in-process inventory represented by the growing plants. This cost is about 20% of the costs shown in Figure 1 for conifers grown on 5-year harvest cycles. It is nearly 40% of the 10-year harvest cycle costs, and 50% of the 15-year cycle costs.
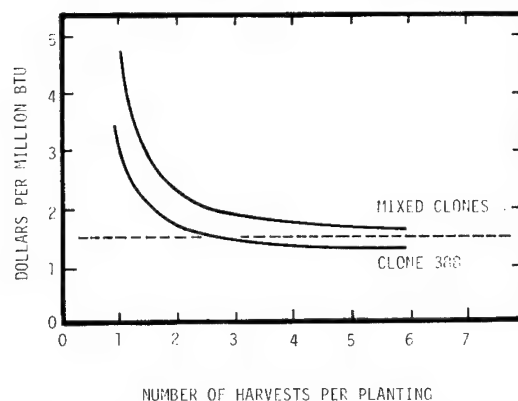
FIG. 2. Estimated cost of fuel value from hybrid poplar (central Pennsylvania data).

The advantages offered by perennials over annuals, however, are crucial to the feasibility of Energy Plantations. Perennials can be harvested essentially throughout the year in response to the demand for fuel, whereas annuals must be planted and harvested on nature's schedule. This means that in those localities where only one annual crop per year is possible, which is the case for most of the United States, a harvested product inventory equivalent to at least a year's supply of fuel will have to be established at harvest time if the Btu Bushes are annuals. Storing and preserving such an inventory would be a substantial and costly proposition. Perennials, on the other hand, preserve themselves until they are reaped. Moreover, in actual practice, the inventory would have to be substantially more than a year's supply to protect against the effect of a poor crop year, if the species grown are annuals. With perennials, the effect of a poor year is likely to be averaged out over the several years required to produce the energy crop.

Certain deciduous trees, such as poplars and a number of others, exhibit rapid juvenile growth and have the added advantage of sprouting vigorously from their stumps after harvesting. Regrowth from the stump means that several fuel harvests can be taken per planting, which is a source of considerable cost economy. Only one harvest can be taken from most conifers. Moreover, by judicious selection of the planting density and harvest schedule, fuel value yields equivalent to converting 0.6% of the solar radiation incident on the growth site can be achieved almost anywhere in the United States where rainfall is 15 in. or more a year and the surface has a soil covering a few feet deep.

Representative estimated costs of fuel derived from hybrid poplars are shown in Figure 2. These estimates are based on harvest yields reported from a number of stands grown by vegetative reproduction from clones on abandoned farms in central Pennsylvania [6]. Similar yields are reported for hybrid poplars and other fast-growing deciduous species in Kansas, Wisconsin, the South, and in other widely distributed localities in this country.

The cost estimates summarized in Figure 2 are based on a planting density of 3,700 plants/acre, and a harvest every 3 years. The assumptions made with respect to the cost of field operations and supplies are the same as those made for the conifer cost estimates previously discussed. The estimated costs shown are for

TABLE IV
Energy Plantation Land Area Required for a 400 MW Generating Station Operating at 34% Thermal
Efficiency and 55% Load Factor

Insolation Rate Btu/ft²-day	Area Required – Square Miles Solar Energy Conversion To Fuel Value		
	0.4 %	0.6 %	0.8 %
1,200	390	260	195
1,300	365	245	180
1,400	340	225	170

harvested and chipped fuel product loaded on trucks ready for transport from the harvesting area. The upper line based on an unselected mixture of poplar hybrids indicates a cost of fuel between about \$1.60 and \$1.80/million Btu of useful fuel value on a schedule involving 4 to 6 harvests/planting. The lower line, based on a hybrid (Clone 388) which is better suited to the locality, indicates a cost between about \$1.25 and \$1.45/million Btu on a 4 to 6 harvests/planting schedule. This cost range can be achieved broadly in the United States and, despite the fact that the Energy Plantation technology is only at the foot of its learning curve, is already substantially lower than the present cost of fuel oils and only moderately above the cost of coal in many parts of the country. It represents a fuel production equivalent to about 120 million Btu/acre/year, and conversion to stored fuel value of about 0.6% of the sunshine falling on the plantation site. In those parts of the country where warm-season perennial grasses flourish, as Bermuda grasses do in the southern tier of states for instance, similar fuel yields at comparable cost can be achieved by harvesting 3 or 4 times a year.

It is evident that certain deciduous tree species grown on short harvest cycles in dense plantings, and any of several warm-season perennial grasses where the climate is suitable, are the preferred Btu Bushes for Energy Plantations. They will require replanting only once every 12 to 20 years and will provide a number of harvests/planting. Moreover, they can be planted with little soil preparation other than shallow disking. Thus, Energy Plantations can be established on land having slopes too steep or soil too chirty or stoney to permit the more intensive soil preparation customarily given land used for intensive farming. As a matter of fact, most of the land which will be used for Energy Plantations is classified by the Department of Agriculture as forest grazing land and grassland range. Much of the land in these categories has little regular use at present. In any event, Energy Plantations will not require land suitable for dirt farming, or tree farming, or that included in the national parks and forests or wilderness areas.

Some may be concerned about the land area required for Energy Plantations, but they need not be. Consider the land required to keep modern pulp mills supplied with pulpwood. In the South at the end of 1971, there were 26 pulp mills each of whose capacity was 1,000 tons of pulp/day or greater. A 1,000 ton/day pulp mill requires about 350 square miles of pulpwood forest to supply it perpetually with wood. An area this large, as is shown in Table IV, is about adequate to supply a 400 MW electricity plant operating at a relatively low thermal efficiency for a modern installation (34%), and at the national average load factor for public

utilities (55%), at only a 0.4% solar energy conversion rate. A 400 MW electric plant is adequate to supply the electricity needs for about 200,000 people at present consumption rates. As a matter of fact, to supply the fuel from Energy Plantations for all the generating capacity presently installed in this country would require less than 160 million acres, even at the rate of conversion of solar radiation to fuel value as low as 0.4%. This area is about a third of the land potentially suitable for Energy Plantations enjoying at best only marginal use at present in this country.

This comparison, involving the total fuel requirements of the utilities in the United States, is not made with the idea that all utilities should be converted to Energy Plantation fuel. It is made only to show that meeting the land requirements for producing Energy Plantation fuel in considerable volume is not beyond the realm of possibility in this land, and to indicate that Energy Plantation fuel production will not be prevented from becoming a major future source of energy in this country because of a limitation imposed by the amount of land available.

CONCLUSION

Fuel value can be produced in this country in Energy Plantations at a cost already competitive with that of fuel oils and increasingly so with that of coal in the next few years.

Energy Plantations are an inexhaustible store of solar radiation from which the energy can be released with high thermodynamic availability.

Energy Plantation fuel has many fundamental advantages over the other present and possible future energy sources with respect to: 1) the national interest; 2) environmental wholesomeness; 3) absence of new potentially catastrophic hazards for mankind; and 4) assurance of future energy supply.

The technologies required for collecting, storing and using the fuel are understood and at hand.

REFERENCES

[1] Alfalfa: R. C. Suter, *Doane's Agricultural Report,* 1972, p. 185. Reed Canary Grass: *Doane's Agricultural Report,* 1972, p. 192.1. Bermuda Grass: B. D. Doss et al., *Agronomy J., 54,* (1962). Corn Silage: G. W. Woodwell, *Sci Amer,* September, 1970, p. 64–72. Forage Sorghum: W. L. Fowler, private communication, June, 1974. Sugarcane: ibid., and *Statistical Abstract of The United States,* 1972 Edition, Table 1024. Gen. Agriculture: G. W. Woodwell, *Scientific American,* September, 1970, p. 64–72. Hybrid Poplar: T. W. Bowersox, private communication, June 1974. Sycamore: R. G. McAlpine, Establishment Report for Sycamore Spacing and Field Study, Forest Sciences Laboratory, U.S. Forest Service, Atherns, Georgia, FS-SE-1107, ATM 45, 1967. Southern Pine: D. H. Dawson, private communication, June, 1974.

[2] "Machinery Custom Rates Guide", *Doane's Agricultural Report,* April, 1974, p. 303.

[3] George C. Szego and Clinton C. Kemp, "Energy Forests and Fuel Plantations", *Chemical Technology,* May, 1973.

[4] Monthly Report of Cost and Quality of Fuels for Steam Electric Plants for April 1974, Bureau of Power, Federal Power Commission, August, 1974.

[5] D. H. Dawson, private communication, June, 1974.

[6] T. W. Bowersox, private communication, June, 1974.

ANNUAL CROPS—A RENEWABLE SOURCE FOR CELLULOSE

DWIGHT L. MILLER

Northern Regional Research Laboratory,
Agricultural Research Service, U.S. Department of Agriculture,
Peoria, Illinois 61604

SYNOPSIS

Historically, cellulosic materials from annual crops have been of major industrial importance. They predate wood for paper by centuries. As early as 500 B.C., pressed sheets were made in Egypt from papyrus. The technique of papermaking, most closely related to processing now followed, was based primarily on cellulose from such annual crops as cotton, flax, and hemp. Commercially, cellulose is available from annual fiber crops, byproducts, and residues. Typical fiber crops are kenaf, jute, reeds, hemp, cotton, and esparto grass. They may be grown under either cultivated or natural conditions. Byproducts include cereal straws, sugarcane bagasse, oilseed stalks, and similar cellulosic materials normally associated with a principal agricultural crop. Residues represent many different types of materials and are best typified by food and animal wastes. Annual crops have increasing potential as renewable raw materials to meet future requirements for cellulose and cellulose-based chemicals.

INTRODUCTION

The efficiency of U.S. agriculture has advanced so fast that for several decades annual crop production has exceeded market demands, except in times of international conflicts or temporary emergencies. Average farm output per acre has increased about 85% since 1940 because of better yielding seeds and greatly improved farming techniques. This increase has exceeded domestic population growth. Even though less acres are planted to meet domestic needs, more crops are still available for export [1] (see Figs. 1 and 2).

A 1974 USDA study [2] projects that requirements for cropland will remain relatively constant beyond the year 2000 even with increased exports. Undoubtedly, total production from all available land could be consumed throughout the world if all were given away. Methods to carry out such a program within the world economic systems are outside the scope of a technical discussion.

Normally, U.S. agriculture first provides food, feed, and fiber, and these outlets usually bring the highest financial return. This will probably always be true. Almost all annual crops produce large amounts of cellulose either in the crop itself or in the byproduct residues remaining after the primary crop has been harvested.

21
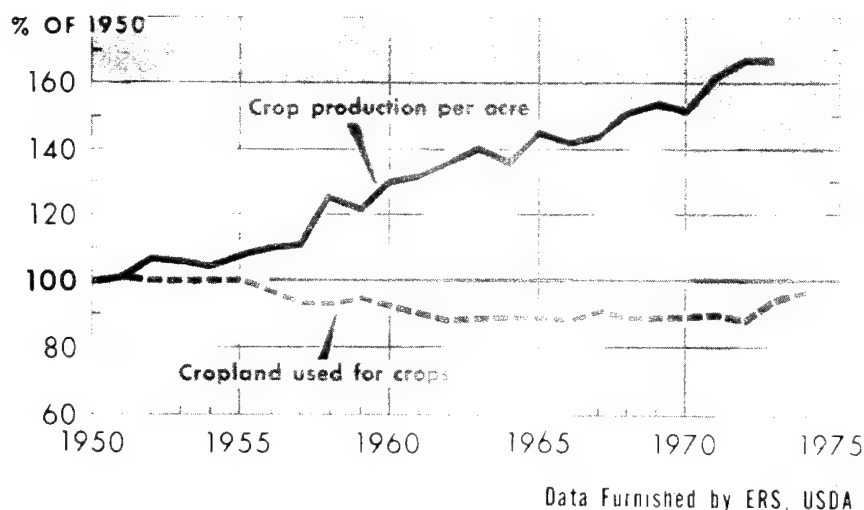
FIG. 1. Annual crops.

Much of these high cellulosic materials can be exploited for the production of such manufactured products as paper and paperboard, for use as chemical raw materials, and for a source of energy. They are annually renewable and they will undoubtedly be available for the predictable future. Two types of cellulosic materials will be considered; namely, cellulosic byproducts and residues from annual food, feed, and fiber crops, and annual nonwood crops high in cellulose.

In the United States little cellulose from annual crops is now used to make pulp or to manufacture chemicals. About 1% of North American fibrous raw material is from byproducts—mostly from sugarcane bagasse. Essentially, no annual fiber crops are commercially grown specifically for this purpose. However, existing byproducts are available and do represent a major potential source of fiber. Their use awaits only the economic necessity.

Agricultural fibers as a whole differ characteristically from woods in chemical composition and fiber dimensions as may be expected from the vast number and variety of annual plants. Many exceptions to these generalizations occur. Typi-
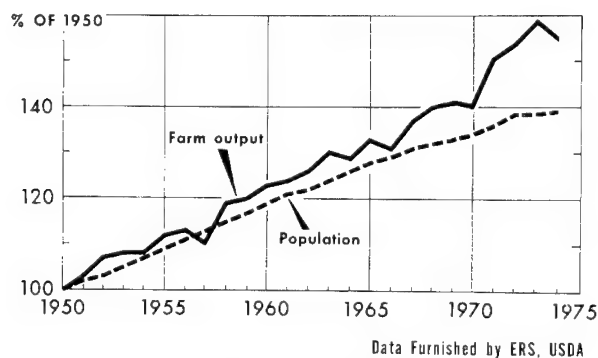
FIG. 2. Farm output and U.S. population.

TABLE I
Typical Dimensional and Compositional Characteristics
of Selected Pulpwood and Nonwoody Plants

Species	Fiber Length, mm	Fiber Width, μ	Crude Cellulose Content, %	Alpha-Cellulose Content, %
Coniferous woods	2.0–5.7	32–44	60	39–45
Deciduous woods	0.6–1.9	38–50	45–62	38–49
Nonwoody plants:				
Sugarcane bagasse	0.3–3.4	9–45	48–58	30–37
Cereal grain straws	1.1–1.5	9–13	43–54	29–39
Bamboo	1.1–3.8	12–22	44–62	30–43
Esparto grass	0.5–3.5	7–18	49–50	33–38

cal dimensional and compositional characteristics of selected woods and annual nonwoody plants are listed in Table I. Note that the cellulosic content of nonwoody plants is usually comparable to, or somewhat lower than, most woods. Of course, there is more variance in the cellulosic content, which ranges from 25 to 60% total cellulose and from 15 to 40% alpha-cellulose. Fiber dimensions are similar. In general, practically all nonwood cellulose from annual crop varieties can serve as raw materials for the manufacture of either paper and paperboard or chemicals.

Of the approximately 2,264 million acres of land used in the 50 states about 475 million acres is classified as cropland (Fig. 3). An additional 604 million acres is classified as grassland. Almost all the idle cropland could be exploited through cultivation to grow annual crops. Possibly some of the grassland could also serve this purpose. On an average, about 300 million acres of cropland has been cultivated for the past two decades. This acreage is slightly lower than that several decades ago. Whether the trend will continue under present world conditions remains to be determined. However, there is now significant unused cropland available on which to grow cellulosic annual crops and there probably will be for many years to come.

Historically, nonwoody cellulosic annual crops have been of major importance.

Data Furnished by ERS, USDA

FIG. 3. Land use.

FIG. 4. Cereal straws (wheat, rye, rice, oats, barley).

They were first used in the manufacture of paper, and they predated wood for paper by centuries. As early as 500 B.C. pressed paper-type sheets were made from papyrus in Egypt. The technique of papermaking most closely related to the processing now followed originated about 105 A.D. in China and was based primarily on fibers from such annual crops as cotton, flax, and hemp.

World production of nonwood plant fiber pulp is more than 7 million tons, or about 5% of all pulp production [3]. Nonwoody fiber includes about 1.1 million tons of bagasse, 2.2 million tons of cereal straw, 1.5 million tons of bamboo, and 0.5 million tons of cotton linter. Other commercial pulping operations are based on esparto, sisal, flax, hemp, abaca, reeds, and sabai grass. Total potential world

FIG. 5. Square-bale rick of wheat straw at mill site after being partially covered with a tarpaulin.

availability of nonwood plant fibers could now exceed 1.5 billion tons annually, of which more than 200 million tons might be readily collected in the United States alone. Even small percentage would be significant in the world's pulp supply.

BYPRODUCTS AND RESIDUES

The present and potential supply of U.S. cellulosic byproducts from domestic crops is not accurately known. The total certainly exceeds 500 million tons (dry basis) of which potentially collectible cereal straws make up about 130 million tons and bagasse more than 5 million tons. Most cereals produce in the order of 2 lb straw/lb grain. General distribution of cereal straws throughout the various States is pictured in Figure 4.

The importance of raw material collection must be emphasized. Modern farming practices for most annual crops require highly mechanized field processing equipment. Minimum transportation of byproduct materials is involved. Most straws, hulls, stalks, cobs, and other byproducts are left in the field. They have some fertilizer value in certain regions, but in areas where they cannot be plowed under or burned, they cause serious disposal problems. The old familiar straw stacks and corncob piles have essentially disappeared from the landscape. The developing farming techniques that use no-till or minimum-till planting may necessitate some increased removal of byproducts from the fields. There is considerable controversy at present concerning collection of cellulosic materials as a separate operation and also about the amounts that can be economically recovered. Any major increase in the use of straw and other byproducts will require major efforts to collect, handle, transport, store, and deliver them at the plant at a cost so that they will be competitive with such other raw materials as hardwood. This effort will possibly mean major engineering breakthroughs. Bulk handling of bagasse and bulk handling and storage of wood chips typify such techniques. At one time, in the United States alone, there were at least 50 pulp mills based on straw, primarily from wheat (Figure 5). More than 650,000 tons of pulp were produced annually from wheat straw in 1950. Today, only a small amount of flax straw is pulped in the U.S. for speciality uses.
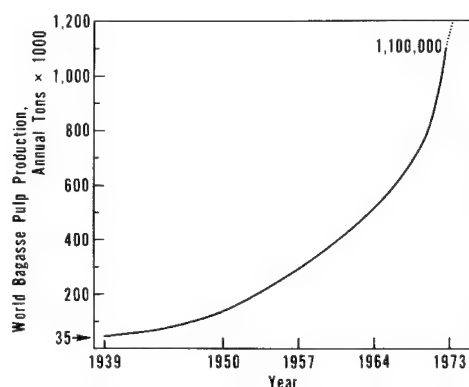
FIG. 6. Bagasse pulp production worldwide.

TABLE II
New Crop Opportunity

Of the 250,000 botanical species:
    From 80-90 produce crops in U.S. worth more than $1,000,000
    Only 200-300 used for commercial crops

Past efforts largely agronomic and to generate new varieties

Chemical composition of plant kingdom largely unknown

Bagasse is still available in collection form. In 1939, the first successful bagasse pulp mills started operation. In 1973, bagasse pulp was produced in some 80 mills located in 22 countries (Fig. 6). One paper mill and one board mill are located within the continental United States.

ANNUAL FIBER CROPS

In the U.S., production of annual nonwood cellulosic crops for industrial use has received little attention. Undoubtedly, this situation is changing because extensive research is now in progress.

There are at least 250,000 known plant species in the world (Table II). Almost all of these are nonwoody annual varieties and almost all contain considerable cellulose. The potential for new commercial crops from them is practically unlimit-

FIG. 7. Kenaf field.

ed. Throughout the ages, man has rather arbitrarily selected the plants that best fill his needs for food, feed, and fibers.

Through research, high-yielding annual crops that convert solar energy can undoubtedly be developed. A significant breakthrough would have major effects on land usage and on world economics. Today, solar efficiency of practically all annual crops is less than 1%. Here again, extensive research is under way to develop crops that better utilize this energy. It is renewable energy and should be available for the foreseeable future.

In 1957, the U.S. Department of Agriculture initiated a new crops program. Its primary purpose was to find crops with major plant constituents different from those already available and to emphasize their potential for industrial use. Included was research on fiber crops for the production of pulp and paper. More than 500 species of fiber plants have now been evaluated. Highest rated materials include kenaf, roselle, sorghums, bamboo, and crotalaria.

Kenaf appears to have the greatest potential as a papermaking fiber. Yields in potential growing regions have been much greater than wood with 10 tons of dry matter/acre/year regularly reported. Under the best conditions as much as 20 tons has been reached (Fig. 7 and 8).

Kenaf has been grown as a fiber crop in parts of the world as a raw material from which to manufacture twine and rope. The bast fiber (about 20% of the total dry stalk weight) is used. Labor and handling costs in the U.S. require that modern cultivation and harvesting techniques be followed, and the whole kenaf stalk must be used if kenaf is to become commercially available. This is the basis for current research efforts.

Kenaf is now under intensive agronomic and utilization investigation by government and industry. Undoubtedly, kenaf or similar stem plants, such as roselle,
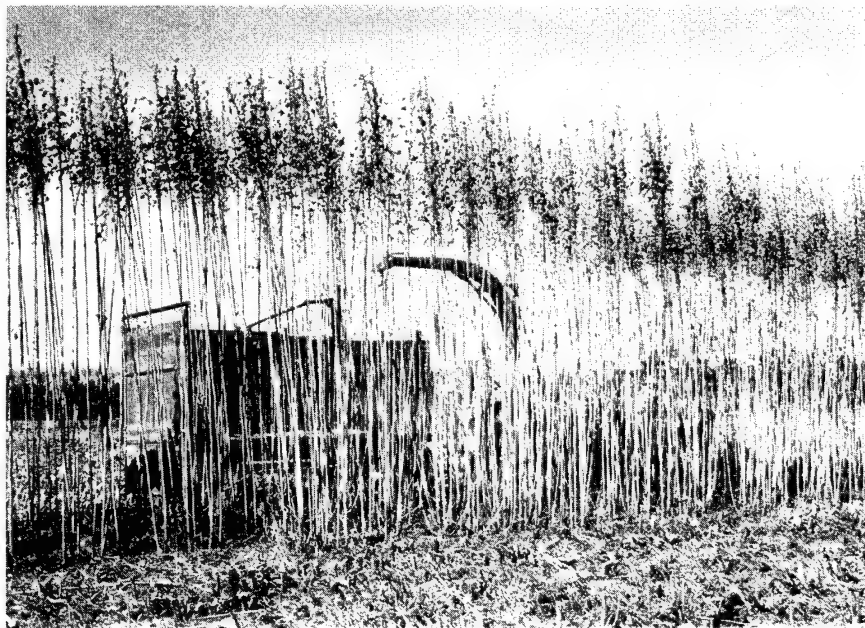
FIG. 8. Kenaf harvesting.

sorghum, or crotalaria, will become important annual cellulosic raw materials in the U.S. and in developing countries. They may be used either by themselves or as blending pulps for wood or with other nonwoody plant fibers, such as bagasse and straw.

CONCLUSION

This review has described briefly the possibilities for renewable annual crops as cellulosic raw materials. The potential now exists with greatly increased production possible. In 1970, the TAPPI Nonwood Plant Fibers Committee was established in recognition of the growing worldwide importance of this agricultural source.

Annual crops should not be considered as a complete replacement for wood as a source of fibrous raw materials. Rather, they have potential for extending limited wood supplies and for contributing desired characteristics and properties to finished products. Their utilization also provides a means to better utilize agricultural production with major resource and energy savings.

REFERENCES

[1] "Handbook of Agricultural Charts," U.S. Dept. Agriculture, No. 477, 1974 p. 17.
[2] "Our Land and Water Resources. Econ. Res. Serv., U.S. Dept. Agriculture, Current and Prospective Supplies and Uses," Misc. Pub. No. 1290, 1974.
[3] J. E. Atchison, presented at the XV Congress of the International Society of Sugar Cane Technologists, Durban, South Africa, June 13–29, 1974. (Reprints are available from Joseph E. Atchison Consultants, Inc., 30 East 42nd Street, New York, New York 10017.)

PROJECTION OF WORLD DEMAND AND SUPPLY FOR WOOD FIBER TO THE YEAR 2000

J. L. KEAYS

Department of the Environment,
Canadian Forestry Service,
Western Forest Products Laboratory,
Vancouver, British Columbia, Canada V6T 1X2

SYNOPSIS

It is estimated that within approximately 25 years world demand for paper and paperboard will be in excess of 400 million metric tons per year. In addition, substantial amounts of comminuted wood will be required for dissolving-grade pulps, fiberboard and the composite boards. By the year 2000, the supply of wood available for use by the present conventional practices of forest harvesting will be of the order of 200 million cubic meters per year short of demand. Various ways in which additional wood fiber might be made available are discussed. The most practical additional source of fiber will come from a more complete utilization of the world's forests already in use. Application of the concept of full-forest harvesting would increase the amount of wood fiber available from world forest resources by 50 to 100%. This would represent an increase of potential fiber which is multifold that of the projected fiber shortfall. Full-forest harvesting is also discussed in terms of the amounts of bark and foliage which will be made available for use.

INTRODUCTION

The primary purpose of the present paper is to consider future demand for fiber products—pulp, paper, paperboard, fiberboard and particle boards. A secondary purpose is to examine the potential sources of raw material which will be required to produce the projected tonnages. The problem of raw-material supply and demand for fiber products cannot be considered in isolation. Most of the raw material for fiber products will come from the forests, and there will be other and increasingly heavy demand on that resource. There will be continuing demand for lumber [6], plywood, solid wood products, and fuelwood—the traditional forest products. In addition, the forests may be called upon to provide raw material for chemicals, for protein, and to augment nonrenewable fuels whose reserves are dwindling and whose costs are increasing at an accelerating rate.

In the following section, future world demand for paper and paperboard is analyzed, and an estimate is made of total wood demand based on its use in the tradi-

29

tional forest products. Based on additional wood needs, this estimate is probably low. An estimate is made of the amount of wood likely to be available for conversion, based on traditional practices in forest harvesting. These estimates indicate that there will be a substantial shortfall. The question of how this shortfall can be overcome is considered in terms of the broad concept of full-forest utilization. Application of this concept, in turn, will provide a whole new spectrum of opportunities for expansion of more efficient and more sophisticated use of the world's forests.

FUTURE DEMAND FOR PAPER AND PAPERBOARD

Background

The question of future world demand for pulp, paper and paperboard involves a complex network of factors—economic, technological, social, and cultural. Many of the factors making up this network support a thesis of continuing and increasing demand for wood-fiber products. These factors include:

1) The large number of end-products derived from wood fiber, including something over 150 major categories of paper and paperboard [14]. The replacement of wood fiber in any one category by substitute materials or methods would not have a major effect on the total demand for wood fiber.

2) The relative freedom of many wood-fiber products from serious erosion by competitive products or raw materials. Personal papers might serve as an example. The probability is vanishingly low that materials will be developed which could serve as a substitute for wood-derived fiber in the manufacture of most personal papers. The probability is equally low that such materials, if developed, could be competitive in price with the products presently derived from wood fiber.

3) The lack of viable substitutes for paper-dependent communications systems. There are many means of communication other than the conventional ones. These include [22]: a) unlimited point-to-point television communications via artificial satellite; b) limited point-to-point transmission of correspondence via communications satellite from a central transmission station; c) widespread use of microfilm libraries; d) tape or microfilm facsimile delivered directly to the home as a substitute for the conventional newspaper; and e) direct television transmission of the contents of any newspaper, sent out from a central news-transmission center. Some of these possibilities, such as limited point-to-point communications via artificial satellite and through receiver-sender stations, could well involve the use of more paper rather than less. This would depend upon how many individuals in the communications chain decided that they should write the message down, or have multiple copies filed.

4) Increasing literacy throughout the world. There is a low per cent market saturation for communications papers in all but a few areas throughout the world [1]. Without a sustained supply of the means by which people can read and write, literacy could not be sustained.

5) Widespread and increasing application of wood-fiber products to man's

knowledge, comfort, well-being, and sense of identity. More people are being served, and an increasing number of end-products are being developed to satisfy man's changing social and economic needs. A typical example would be the rapid expansion of markets for disposable paper products [3–5,7,13,41,47,57]. Highly developed societies may well go through an extended period in which the cost of a new wood fiber dress for utility wear might be less than the cost of cleaning an old one—if the new dress comes from a low-cost, renewable raw material, and the total fuel costs for cleaning are sufficiently high.

It would be difficult to overemphasize the point that the use of wood-fiber products is complex in the extreme and is becoming more so. It is tightly woven into the total fabric of man's learning, technology, use of leisure time, cultural development, life styles, changing priorities, and the shrinking wells of raw-material resource.

What are the past and present dimensions of fiber-products consumption, and how may these dimensions be expected to change through the present century?

Long-Range Demand Based on "Critical Year"

From 1950 to 1970, world production of paper increased threefold, from 40 to 130 million tons* per year [17]. Table I gives the long-range potential demand for paper and paperboard to the point where demand levels off [25].

TABLE I

Future World Demand for Paper and Paperboard Based on the Concept of "Critical Year" [25]

Year	Assumed growth rate, %	Potential world demand for paper and paperboard in millions of tons [a]
1965	5.00	100
1970	4.90	120
1975	4.80	150
1980	4.70	190
1990	4.50	280
2000	4.30	400
2010	4.10	570
2020	3.90	800
2050	3.30	1,800
2100	2.30	4,600
2150	1.30	9,800
2200	0.30	16,000

[a] All values rounded out to two significant figures.

* Throughout this paper the unit ton(s) denotes the metric ton: 1 ton = 10^3 kg = 2200 lb.

The figures shown in Table I are probably somewhat low for the short term (to the year 2000) and unrealistically high in the long term (beyond, say, 2050). They do indicate, however, before the turn of the present century, that world demand for paper and paperboard will be *multifold* what it is today, and in the long term potential demand will far exceed potential fiber supply as defined by conventional practices of forest harvesting.

Demand Based on Historical Trends

Assumptions

Several basic assumptions have been made in the present analysis:
1) The period from 1950 to the present is a satisfactory time basis in estimating trends in paper and paperboard demand.
2) Past historical trends in paper and paperboard consumption will continue. A large number of indicators have been used [26,49] in projecting demand for paper and paperboard, but there is no convincing argument that any one component indicator is to be preferred over the others.* Paper and paperboard consumption is dependent upon clusters of interacting variables, including: a) population and population distribution; b) total gross national product and its composition; c) disposable income and its distribution; d) literacy and education levels; e) social custom and usage; f) population mobility; g) method of mass transport; and h) prestige symbolism.

Some of these clusters of variables, such as literacy and educational level, may be susceptible to analysis in terms of paper and paperboard demand; other variables, such as prestige symbolism, are not.

Past experience has shown that the paperboard and fiber-products field is in a state of constant flux: markets for conventional products increase slowly or rapidly, they remain static, decrease slowly, or they disappear; new products are created and old products are modified.

To some extent, all projections dealing with a subject as complex and multicomponent as paper and paperboard use, must have a strong intuitive or subjective component. In one sense, the problem is a simple one. The sum total of economic, technological, competitive, sociological and cultural pressures and judgments relating to the demand for paper and paperboard has produced a consumption-time curve of given shape. The analyst must make a subjective judgment in answering the question: "Will the sum total of all factors operative over the next 25 years result in a continuation of the consumption-time trend of the past 25 years?" In the present analysis, the answer to this question is assumed to be "yes."
3) Projection for total demand for paper and paperboard is as reliable as the summation of individual projections for each of the major paper and pa-

---

* There is one potential weakness in the use of secondary indicators, such as per capita consumption. Any errors in the secondary indicator show up in the total demand projection and, the more secondary indicators that are used, the higher the probability of error which may be cancelling or cumulative. If the per capita use of a product is underestimated (which is easy to do in a technologically dynamic society), and the demographic projection is unrealistically low (which it frequently is), or if critical factors are omitted, then the projection for total consumption obtained by summing may be seriously in error.

perboard categories. This was found to be true for projection of demand for the major paper and paperboard categories in the United States [26].

4) Graphic analysis, or simple curve extension, is a satisfactory method for curve extrapolation to future paper and paperboard demand, and gives as realistic a projection as can be obtained by more elaborate analyses of the data available.

Projection

As shown in Figure 1 and Table II, graphic projection of historical trends in paper and paperboard consumption gives a demand estimate of 415 million tons per year by the year 2000. The statistics upon which this extrapolation is based are given in Table III.
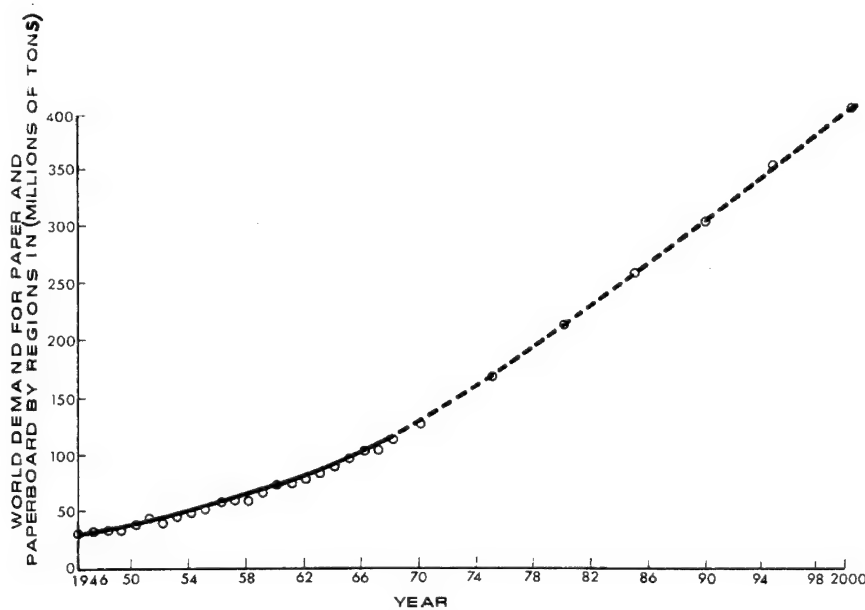
FIG. 1. World demand for paper and paperboard to the Year 2000.

TABLE II
Projected Future World Demand for Paper and Paperboard

Year	Demand in millions of tons
1975	165
1980	210
1985	252
1990	300
1995	355
2000	415

TABLE III
World Production of Paper and Paperboard

Production year	World production of paper and paperboard (in millions of tons per year)(15,17)
1951	44
1952	42
1953	48
1954	51
1955	58
1956	60
1957	62
1958	63
1959	69
1960	74
1961	78
1962	81
1963	86
1964	92
1965	97
1966	105
1967	106
1968	115
1969	127
1970	130
1971	131
1972	141
1973	155

Projection Based on Consumption Trends in the United States*

The projected demand for paper and paperboard in the United States by 2000 is 134 million tons. (This value is somewhat higher than recent projections for future paper and paperboard demand in the United States [46,48].) By that time, the United States's consumption of paper and paperboard is estimated to be 32% of world consumption. On this basis, world demand would be 420 million tons.

Projection of Demand by Regions

Figure 2 and Table IV indicate future paper and paperboard consumption by major economic regions [53]. It is considered no more than accidental that the individual estimates total to 415 million tons. Long-range projections derived from the values given in Table IV are questionable because 25 years is too long an extrapolation period for the data available, and because the values shown for some regions are based on too limited data.

Creditability of Forecast

The estimated potential world demand for paper and paperboard of 415 million tons per year by 2000 does not mean that the consumption is expected to be pre-

* Because of space limitations, the detailed analysis upon which the above values are based is not presented here.

cisely this value in the single year 2000. Rather it means that, within a few years from the end of the present century, world demand level for paper and paperboard will be around 400 million tons [8,9,12,19,44,54]. An analysis of previous projec-
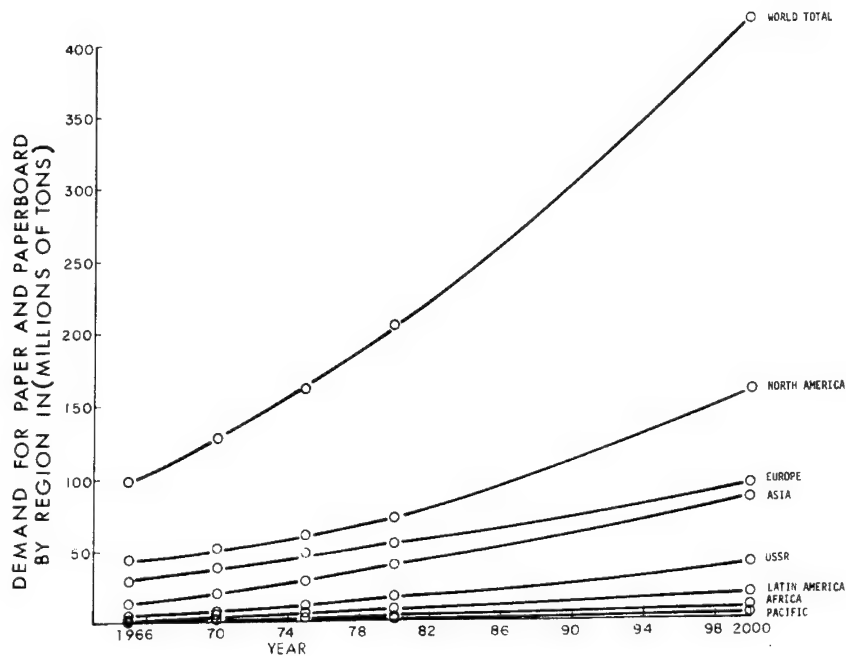
FIG. 2. World demand for paper and paperboard to the Year 2000 by major regions.

tion analyses in this area would suggest that the value of 415 million tons per year derived in the present analysis may well be low, by perhaps 10 to 20% (Appendix I).

TABLE IV

World Demand for Paper and Paperboard to the Year 2000 by Major Regions [53]
(in millions of tons)

Region	1965	1970 (est.)	1975 (est.)	1980 (est.)	2000 [a]
North America	43.6	52.3	61.7	72.0	150
Europe	28.7	37.9	47.6	59.3	95
Asia	14.3	20.6	29.0	40.3	85
USSR	5.3	8.3	12.4	18.1	50
Latin America	3.4	4.8	6.7	9.4	20
Africa	1.2	1.7	2.5	3.6	10
Pacific	1.3	1.5	1.9	2.4	5
World Total	97.8	127.1	161.8	205.1	415

[a] Extrapolation of values in reference [53].

DEMAND FOR OTHER FIBER PRODUCTS

Dissolving Pulps

Traditionally, dissolving-grade pulps have been about 5% of total world pulp production [16]. An analysis of trends over the past 20 years indicates that this percentage is slowly dropping. On this basis, production of dissolving-grade pulps by 2000 is assumed to be 16 million tons per year, or 4% of total paper and paperboard production.

Fiberboard and Particle Boards

Table V shows the trend in fiberboard and particle boards production over a 10 year period.

TABLE V
Production of Fiberboard and Particle Boards [17]

Year	Production millions of cubic meters			Production of fiberboard and particle boards as % of total
	Plywood	Fiberboard	Particle boards	
1961	16.5	4.7	3.5	33
1966	25.3	6.3	9.9	39
1970	32.6	7.8	18.1	44

Table V shows the high growth rate of fiberboard and particle boards and indicates the trend for these products to replace plywood.

An analysis of the factors relating to long-term demand for plywood, lumber, fiberboard and the composite panel products, by Dr. M. N. Carrol (Western Forest Products Laboratory, Vancouver, British Columbia), suggests a compounded growth rate of the last two combined of 7% per year. Extrapolating this growth rate to 2000, this would give the following indices:

Production of fiberboard and particle boards by 2000	230 million cubic meters
Yield (based on raw material to a plant)	90 %
Production of uncut and unsanded board	250 million cubic meters
Average specific gravity of products	0.8
Weight of uncut and unsanded board	200 million tons
Average specific gravity of wood used	0.5
Wood requirements (200/0.5)	400 million cubic meters

TOTAL WORLD DEMAND FOR WOOD FOR FIBER PRODUCTS

From the above projection of demand for fiber products, the wood required can be determined as shown in Table VI.

TABLE VI
World Demand for Fiber Products by 2000

Product	World demand (millions of tons)	Product yield %	Wood requirements	
			Millions of tons	Millions of cu. m
Dissolving pulps	16	35	46 [a]	120 (approx.)
Paper and paperboard				
Total	415			
Pulp required [b]	332			
Wood pulp required [c]	315	60	525 [a]	1,310
Fiberboard and particle boards	200	—	— [d]	400
			Total	1,830
			Round out to	1,900

a Specific gravity of wood assumed to be 0.4.

b Use of recycled fiber and fillers assumed to be 20%.

c Wood is assumed to constitute 95% of the raw material used in the manufacture of paper and paperboard [16].

d Specific gravity of the wood assumed to be 0.5 (mainly hardwoods used).

TOTAL WORLD DEMAND FOR WOOD*

It is estimated that the total world demand for wood by the year 2000 will be not less than 4,000 million cubic meters, compared with the total cut of approximately 2,400 million cubic meters in 1972. The predictability factor is believed to be low in the case of total wood requirements. The reliability of production statistics for many wood products is low and data are incomplete [2,45]. Although the projection for total world demand for wood may not have a high creditability factor, the estimate is believed to be quite conservative [19,23,51,52]. The true figure could be appreciably higher than projected, but it is not expected to be lower, particularly in the light of possible increased use of wood for fuel [24], chemicals [20,37] and animal food supplements [37].

FUTURE SUPPLY OF WOOD ABOVE PRESENT CUT

The difference between the projected world demand of 4,000 million cubic meters per year and the present annual cut of 2,400 million cubic meters is 1,600 million cubic meters. There are a number of ways in which this 1,600 million cubic meters can be obtained. The more important of these methods are listed below, in what is considered to be descending order of importance. The relative importance of the various possibilities is made up of a factor of time and a factor of magnitude, and the order in which the possibilities are listed involves some subjective combination of these factors.

* See Appendix II.

1. The exploitation of coniferous forests not presently in use [27,50,55].
2. Closer utilization of all forest resources presently in use [28].
3. Greater conversion of processing wastes from sawmills, veneer plants, and wood-working plants [21].
4. An increase in plantation forests [6,18,28,51,52].
5. Harvesting on a shorter rotation cycle [28,43,51,56].
6. Improved silvicultural practice, land fertilization, genetic selection, thinning, optimum spacing, and irrigation [51].
7. The utilization of wood species, primarily hardwoods, not presently used, or used only as a small percentage of the potential wood supply [32,33,42].
8. Manufacture of stronger pulps, so that the basis weight of a given product can be reduced, or, as in the case of refiner-mechanical pulps, a lower percentage of low-yield chemical pulps are required in a wide range of end products [38,51,52].
9. Increased yield of pulp across the digester [51].
10. Reduction in loss of forest by fire, insects, decay, land alienation, and accidental loss [11,40].

TABLE VII

Potential Sources of Additional Wood Required to Meet Estimated World Demand by 2000

No.	Wood source	Additional wood [a] (millions of cubic meters)
1	Use of unexploited coniferous forests	650
2.	Closer utilization of the world's forests	30
3	Additional conversion of mill wastes	100
4	Increased plantations	100
5	Shorter rotation cycle (included in other categories)	...
6	Improved silvicultural practice	80
7	Increased use of hardwoods	320
8	Development of stronger pulps	50
9	Increased yields across the digester	30
10	Reduction in loss through fire, decay, alienation of forest lands, and other miscellaneous causes	40
	Total	1400

[a] Space does not permit inclusion of the details of the analysis upon which the values shown in Table VII are based, or a listing of the voluminous reference material available [28].

An estimate of the amount of additional wood which might become available by the year 2000 from these potential, traditional sources of wood is given in Table VII.*

* Although the estimates given in Table VII are based on detailed analysis of data available for each of the potential sources of additional wood, the estimates are of necessity speculative and subjective.

If by the year 2000 the additional world wood requirement is 1600 million cubic meters, and the amount apparently available from the traditional sources exploitable on a basis of present-day practice is 1,400 million cubic meters, there will be a potential shortfall of the general order of magnitude of 200 million cubic meters. To place this value in perspective, it is approximately equal to twice Canada's present cut of industrial wood [35].

This shortfall will have to be made up from some combination of: 1) increased use of non-wood fibers, such as bagasse; 2) an even closer utilization of the world's forests than is presently envisaged; 3) silvicultural practices at a higher level of forest yield than are presently anticipated; 4) additional reduction in forest loss through fire, land alienation, wood decay, and miscellaneous causes; 5) utilization of tree components other than the bole; that is, some part of complete-tree utilization; and 6) application of the concept of full-forest utilization, which is discussed in the following section.

FULL-FOREST UTILIZATION

The amount of wood, over and above that suggested in Table VII, which might be or will be secured through use of nonwood fiber, closer forest utilization, improved silviculture, and reduced loss, is probably not high *in toto*. The amount of additional fiber available through complete-tree utilization, that is, from use of components other than the traditional bole [58–62], is vast. From complete-tree utilization alone, as applied to traditional forest harvesting, and applied to the world's forests likely to be in use by 2000, the potential additional fiber recoverable from a more complete utilization of the trees, is of the following order of magnitude:

From the unmerchantable top of the bole (5% of 3,800 million cubic meters [29])	190 million cubic meters
From the branches (10% of 3,800 million cubic meters [30])	380 million cubic meters
From the stump-root system (20% of 3,800 million cubic meters [31])	760 million cubic meters
Total	1,330 milion cubic meters
Round out to	1,300 million cubic meters

The complete-tree utilization concept, applied to 15–20% of the world's forest harvesting practice, could supply the anticipated shortfall of 200 million cubic meters per year.

Application of the concept of full-forest utilization would supply appreciably more fiber. Full-forest utilization is conceived as being "use of all components of all trees in a given forest area" [34,39]. "All components" would include the bole, the unmerchantable top, the branches and foliage, and the stump-root system. "All trees" would include large trees and small trees, trees live and trees killed by fire, decay, insect attack, drowning, or accident. It would include all hardwoods and all softwoods, all standing timber, and such down material as might be removed and processed economically.

TABLE VIII

Additional Biomass Available from Various Forest Types As a Result of Full-Forest Utilization [36]

Forest type	Increase in full-forest harvesting vs. conventional harvesting %	
	Hardwoods	Softwoods
Uniform, even-aged, good sites	35	30
Average mature forests, medium sites	100	60
Mixed, non-uniform, average to poor sites	100 to 300	100 to 200

Recent reviews on the concept of full-forest utilization [34,36,39] have indicated the dimensions of additional biomass recoverable, as shown in Table VIII.

To the values shown in Table VIII can be added another 20% biomass recoverable from harvesting the stump-room system [31,36]. Most of the world's forests would probably come in the second or third of the categories listed in Table VIII. Thus a reasonable expectation of increased yield of biomass from full-forest utilization, compared with conventional harvesting practice, would be 100%. At an annual total world cut of 3,800 million cubic meters, this would mean an additional biomass yield of 3,800 million cubic meters. Almost 65% of this material would be suitable for the manufacture of fiber products and thus the additional biomass from full-forest utilization would give 2,500 million cubic meters of additional wood. The stump-root system would give another 800 million cubic meters of biomass, consisting of 85% wood and 15% bark [31]. Any potential shortfall of wood fiber over the next 20 to 30 years could be made up by full-forest utilization, even allowing for restrictions which may arise from considerations such as soil erosion or nutrient depletion.

OTHER CONSEQUENCES OF FULL-FOREST UTILIZATION

It will be noted that additional material recoverable from full-forest utilization is given in terms of biomass, rather than in conventional terms such as growing stock, inventory, merchantable timber, or wood. The additional material, recoverable from the forest in full-forest harvesting, will be made up of:

Wood suitable for fiber products	65%
Wood best suited to chemical conversion or used as fuel (small twigs and branches, fines, decay)	10%
Bark	15%
Foliage	10%

It is not the purpose of the present review to consider the end uses to which the various components of the forest biomass might best serve. In general terms, bark

will find increasing value as fuel, as a source of adhesives or chemicals, and in a variety of miscellaneous products. That part of the wood not suitable for conversion to fiber products can be used for fuel, chemicals, such as methanol and ethanol, or protein via hydrolysis and fermentation. It would not be possible at the present time to estimate, even approximately, the tonnages of forest biomass which might be converted in the future to fuel, chemicals, and protein. Even a cursory look at the potential world needs for products derivable from man's second most valuable renewable resource, the forest, would suggest that in time, most of the world's forest biomass will be so used.

The entire picture of world supply of, and demand on, the world's forests is changing quite rapidly. Ten years ago there were indications that conventional forest harvesting would not provide tomorrow's needs for the conventional forest products—plywood, lumber, solid products, fuel, and the fiber products. The rapid development of full-forest utilization will provide sufficient material for these conventional forest products beyond the turn of the century. However, new demands upon the forest resource could make even the massive additional raw material supply, made available from the world's forests as a result of full-forest utilization, inadequate to meet new demands and needs.

CONCLUSIONS

A series of arguments are developed in the present paper. These arguments run as follows: 1) the total future world demand for wood will be in excess of the wood likely to be available from the world's forests by present conventional logging or forest harvesting practice, based on the production of the conventional forest products; 2) the concept of full-forest utilization will be applied to an increasing extent in a growing number of areas throughout the world; 3) full-forest utilization will more than make up any anticipated shortfall in wood fiber to meet world demands for wood; and 4) based on potential increased demand for wood for fuel, for chemicals, and for animal food supplements, the demand for wood may be appreciably higher than that anticipated on a basis of the production of conventional forest products only.

As a result of full-forest utilization, there will be available increased amounts of bark, fine material, small branches and foliage not suitable for conventional forest products. These materials, in turn, offer the possibilities of plentiful and relatively low-cost raw material available for conversion to a number of products, including chemicals, fuel, animal feed supplements, and foliage chemicals.

APPENDIX I

Reliability of Forecast World Demand for Paper and Paperboard

One indirect measure of reliability can be obtained from an analysis of previous forecasts for paper and paperboard consumption—by comparing the forecast with the actual consumption figures. In 15 of the 16 forecasts for which data were examined, the projected value was lower than the actual value, the shortfall ranging from 5 to 70%. Consistent projection shortfall would suggest the presence of a systematic error in all forecasting demand for paper and paperboard, since random error would be expected to give either high or low projections. There are a number of obvious reasons why the estimates

are low, including unrealistically low estimates for population growth, increase in Gross National Prod-
uct (GNP), shifting distribution of disposable income, and per capita consumption of paper and paper-
board. Undoubtedly some part of the shortfall results from the conservative nature of economic fore-
casters, who probably believe that it is safer to underestimate than to overestimate.* It is believed that
some fairly large part of the extent to which forecasts fall short of reality arises from a lack of knowl-
edge on which to predict the effect of those technological or social changes which result in increased
consumption of paper. This accounts for perhaps 15% shortfall in projection analyses. On this basis,
the present author would suggest that the true world production of paper and paperboard in the year
2000 might well be, in actual fact, closer to 475 million tons, that is, 415 plus 15%, than to the 415 mil-
lion tons developed in the present analysis.[†] Documentation of the thesis that projection analysis of the
type used does not allow for accelerated innovation in the pulp and paperboard field is beyond the scope
of the present analysis, but a number of examples could be cited illustrating the general principle in-
volved. Where projections for paper and paperboard demand are based on demographic trends, or de-
rived from estimates for trends in GNP, disposable income, etc., it is certain in most cases, and highly
probable in all other cases, that allowance has not been made for a vastly increased demand for dispos-
ables—i.e., bedding, hospital gowns, dresses, curtains, and miscellaneous items of apparel. It is not
possible to predict realistically the future demand for disposables in the form of paper or paper-plastic
or combinations of paper with other fibers, since there are insufficient data for statistical analysis.
However, it is certainly conceivable, and not unrealistically possible, that within 30 years a billion peo-
ple (the combined population of North America, Europe, and the Soviet Union) will consume an aver-
age of 50 pounds per person per year [7,13,41] in the form of disposables. This would amount to 25
million tons of production. In short, the projection for world demand for paper and paperboard by the
year 2000 could be low by 25 million tons, or 6%, because of a single type of development in wood-fiber
use, the effects of which can now be seen only in the faintest outline.

Another example, not related to innovation, but related to a changing society, could be cited in the
field of potential newsprint consumption. If 10 million commuters in the United States were to use
commuter trains, either from choice or from necessity, this would represent 4 billion commuter trips
per year, and if each commuter bought one additional newspaper weighing 1 pound, this would con-
sume an additional 2 million tons per year of newsprint.

In the field of communications papers, if the possession of a library were to become a prestige symbol
(or a cultural necessity), 20 million families each purchasing a thousand pounds of books, would in-
crease book-paper consumption by 10 million tons over 10 years.

There may be, of course, numerous other examples of increased paper and paperboard consumption
resulting from the development of new products or end uses which could only be discussed *a posteriori*
since they have not yet been envisaged.[‡]

* The social advantage of so doing can be questioned, since as much loss to a given economy could
result from something not being done (such as not putting in a mill because of a low forecast of de-
mand) as from what is done (such as to put in a mill which is forced to operate short of productive max-
imum because of an unrealistically high forecast).

† The higher figure has not been used, but there is no reason to suppose that a forecaster is in a better
position in 1975 than he was in 1950 to predict unforeseeable changes in paper and paperboard use. It
might be argued that a simple graphic projection of the production curve for paper and paperboard
would include the missing 15%, since technological and social change has gone into the creation of the
curve on which the projection is based. However, this would assume a constant rate of acceleration,
which is not necessarily a valid assumption.

‡ In the realm of pure speculation, mention might be made of at least one future potential for massive
use of wood fiber. If it were possible to develop from wood fiber a set of dishes which met all the re-
quirements of the user, and which were readily disposable without washing, there might be a market
arising from:

1,000,000,000 people
200 days per year,
2 meals per day,
¼ pound of disposable dishes per person per meal,

to give a total potential market of 50 million tons per year of wood fiber. The saving in fuel required to
heat hot water would be appreciable and the fuel value of the discarded fiber dishes probably even
more so.

APPENDIX II
Total World Demand for Wood by the Year 2000

F.A.O. forecasts for world wood demand by 1975 [2] and an estimate of the demand in 2000 is given in Table IX. The three values shown for South America, Africa, and Asia-Pacific area could be low by as much as 200 million cubic meters, which would give a total estimated world demand by the year 2000 of 4200 million cubic meters. To the extent that these values have been underestimated, it means that the world shortfall for total wood demand will be greater than estimated in the present study.

TABLE IX
World Demand for Wood in Selected Areas (all values in millions of cubic meters)

Area	Cut 1960-62	Industrial wood 1975	Fuelwood 1975	Total wood 1975	Estimate of demand for 2000	Ref. for last col.
Europe	354.6	346	74	420	500	53
N.America	354.8	398	34	432	970(US=610) (Canada=360)	53 10,56
U.S.S.R.	350.6	313	80	393	900	27
S.America	231.1	78	220	298	350	53
Africa	206.2	39	246	285	350 [a]	
Asia-Pacific	633.6	320	545	865	900 [a]	
(Japan)	(75)	(101)	(12)	(113)	(150) [a]	
Total	2131	1494	1199	2693	3970	
Rounded out to	2100	1500	1200	2700	4000	

[a] Estimates based on a number of regional analyses.

REFERENCES

[1] Anon., "World Demand for Paper to 1975," United Nations, F.A.O., Rome, Italy, 1961.

[2] Anon., "Wood: World Trends and Prospects," United Nations, F.A.O., FFRC Basic Study No. 16, 1967.

[3] Anon., *Timber* (Finnish), *19,* 160 (1968).

[4] Anon., *Paper Trade J., 153,* 40 (1969).

[5] Anon., *Paper Trade J., 153,* 74 (1969).

[6] Anon., "Supply of Wood Materials for Housing," United Nations, F.A.O., Vancouver, Canada, 1971.

[7] Anon., *Can. Pulp Paper Ind., 24,* 39 (1971).

[8] Anon., "Outlook for Pulp and Paper Consumption, Production and Trade to 1985," United Nations, F.A.O., Advis. Comm. Pulp Paper, Rome, Italy, 1971.

[9] Anon., *Paper Trade J., 155,* 81 (1971).

[10] Anon., *Can. Pulp Paper Ind., 25,* 25 (1972).

[11] Anon., *World Wood, 13,* 26 (1972).

[12] Anon., *Paper Trade J., 156,* 50 (1972).

[13] Anon., *Paper, 183,* 172 (1975).

[14] Anon., Current Industrial Reports: Pulp, Paper and Board, Series M26A. U.S. Dep. Commer., (selected years).

[15] Anon., Pulp Paper Int., Rev. Number (selected years).

[16] Anon., Wood Pulp Statistics. Pulp Div., Am. Paper Inst., New York, (selected years).

[17] Anon., "Yearbook of Forest Products," United Nations, F.A.O. Rome, Italy, (selected years).

[18] J. E. Atchison, *Paper Trade J., 157,* 34 (1973).

[19] R. C. Andree, *Pulp Paper, 47,* 123 (1973).

[20] S. A. Ballard, *Chem. Ind.,* 1129 (1968).

[21] L. H. Blackerby, *Pulp Paper, 45,* 84 (1971).

[22] A. Clarke, *Horizon, 4,* 17 (1962).

[23] F. P. Doane, Jr., *Paper Trade J., 157,* 23 (1973).

[24] R. S. Evans, Can. For. Serv., West. For. Prod. Lab. Inf. Rep. VP-X-129, Vancouver, B.C., 1974.

[25] J. F. Gaston, "Growth Patterns in Industry—A Re-examination," Nat. Ind. Conf. Board, Stud. Bus. Econo. No. 75, New York, 1961.

[26] D. Hair, "Use of Regression Equations for Projecting Trends in Demand for Paper and Board: with Projections of Demand to 1985 for Major Grades of Paper and Board, Wood Pulp, and Pulpwood," U.S. Dep. Agric., For. Serv., For. Résources Rep. No. 18, Wash., D.C. (1967).

[27] J. L. Keays, "The Forests and Forest Industries of the U.S.S.R.," *Am. Soc. Agric. Eng. Proc., For. Eng. Conf.,* St. Joseph, Mich. 1969.

[28] J. L. Keays, Can. For. Serv., West. For. Prod. Lab., Inf. Rep. VP-X-64, Vancouver, B.C. 1970.

[29] J. L. Keays, Can. For. Serv., West. For. Prod. Lab., Inf. Rep. VX-X-69, Vancouver, B.C. 1971.

[30] J. L. Keays, Can. For. Serv., West. For. Prod. Lab., Inf. Rep. VP-X-71, Vancouver, B.C. 1971.

[31] J. L. Keays, Can. For. Serv., West. For. Prod. Lab., Inf. Rep. VP-X-79, Vancouver, B.C. 1971.

[32] J. L. Keays, Aspen Symp. Proc., U.S. Dep. Agric., For. Serv., Gen. Tech. Report NC-1:4, 1972.

[33] J. L. Keays, J. V. Hatton, G. R. Bailey, and R. W. Neilson, *Can. For. Serv., West. For. Prod. Lab.,* Inf. Rep. VP-X-120, Vancouver, B.C., 1974.

[34] J. L. Keays, *Pulp Paper Mag. Can., 75,* 43 (1974).

[35] J. L. Keays, *For. Prod. J., 24,* 13 (1974).

[36] J. L. Keays, *AIChE Symp. Ser. 146, 71,* (1975).

[37] J. L. Keays, and G. M. Barton, Can. For. Serv., West. For. Prod. Lab., Inf. Rep. VP-X-137, Vancouver, B.C., 1975.

[38] J. L. Keays, and D. A. Harper, "Refiner Mechanical Pulp: End-use Potential," *Pulp Pap. Can.* (in press).

[39] J. L. Keays, and J. V. Hatton, Part I: World Wood Supplies and the Implications of Full-Forest Utilization, *Pulp Paper Int.* (in press).

[40] M. R. Lockman, Can. For. Serv., Inf. Can. Cat. No. Fo 51-2/1969, (1972).

[41] H. Lunk, and K. Stange, *Angewandte Chemie, Ind. Ed.,* 10, 287 (1971).

[42] J. N. McGovern, *Paper Trade J., 153,* 38 (1969).

[43] J. N. McGovern, *Paper Trade J., 156,* 28 (1972).

[44] G. H. Manning, Can. For. Serv., Pub. No. 1327, Ottawa, Canada, 1974.

[45] R. Marty, *J. For., 67,* 88 (1969).

[46] S. U. Rich, "Demand Pressures: Market Demand Prospects for the U.S. Paper Industry During the Next Quarter Century," Proc. Conf. Future Tech. Needs U.S. Pulp Paper Ind., State Univ., N.Y., Coll. Environ, Sci. For., Syracuse, N.Y., 1973, p. 7–13.

[47] S. E. Ross, *Chemtech.,* 535 (Sept., 1972).

[48] B. Slatin, *Tappi, 55,* 499 (1972).

[49] R. J. Slinn, *J. For., 70,* 275 (1972).

[50] J. H. G. Smith, *For. Chron., 44,* 13 (1968).

[51] B. K. Steenberg, *Paper Trade J., 155,* 59 (1971).

[52] B. K. Steenberg, *Pulp Paper Int., 13,* 57 (1971).

[53] T. Streyffert, *World Pulpwood: A Study in the Competitive Position of Pulpwood in Different Forest Regions,* Almquist and Wiksell, Stockholm, 1968.

[54] A. Sundelin, Pulp Paper, World Rev., 1971, p. 16.

[55] D. A. Wilson, "Wood Products—The Supply of Timber from Canadian Forests," presented at Nat. For. Conf., Montebello, Quebec, Feb. 11–24, 1966.

[56] D. A. Wilson, *Commonw. For. Rev., 48,* 136 (1969).

[57] W. G. Wilson, *Paper Trade J., 153,* 28 (1969).

[58] H. E. Young, *Pulp Paper, 48,* 46 (1974).

[59] H. E. Young, *For. Prod. J., 24,* 13 (1974).

[60] H. E. Young, and P. M. Carpenter, Maine Agric. Exp. Sta., Orono, Tech. Bull. 28, 1967.

[61] H. E. Young, and A. J. Chase, Maine Agric. Exp. Sta., Orono, Tech. Bull. 17, 1965.

[62] H. E. Young, L. Strand, and R. Altenberger, Maine Agric. Exp. Sta., Orono, Tech. Bull. 12, 1964.

OUR CHANGING WOOD RESOURCE—ITS EFFECT ON THE PULP INDUSTRY

BRUCE ZOBEL

School of Forest Resources,
North Carolina State University,
Raleigh, North Carolina 27607

SYNOPSIS

The quality and type of wood available to the pulp industry is rapidly changing; manufacturers must plan ahead and learn to use the material becoming available. Rapidity of the change depends on the demand for cellulose products which in part will be determined by the price of petroleum products and coal. Timber supply trends are affected by economic pressures and environmental considerations. They may fluctuate but are likely to become more intense with time. There are numerous reasons for the change in the quality of wood that will be available. Viewed in light of today's technology and quality standard, many of the changes may appear "bad." However, if the quality of the new raw material is planned for, and necessary manufacturing adjustments are made, some of the "bad" features may ultimately be considered "good." Following are some of the reasons why the wood supply of the future will differ from what it is today.

1. Wood available will be young (or juvenile) because of reduced rotation (harvesting) ages, greater use of young thinnings and use of top wood formerly considered to be unmerchantable. Especially in the conifers, this will result in wood with shorter tracheids having thinner cell walls, considerably higher hemicellulose content and increased amounts of compression wood with its greater amount of lignin. Resin content will be lower and paper strength properties different from that made from older wood.

2. Especially in the southeastern United States, wood is being tailor-made for the ultimate product by genetic and silvicultural manipulation. The most useful result will be greater uniformity of wood between trees of the same species. It even appears possible to develop trees with greater uniformity in wood density within the bole of individual trees.

3. Species composition in the forests will change; in the South and West, conifers will predominate while species such as aspen will become more widely available in the Lakes States and Northeast.

4. More complete utilization, which in some cases includes branches and leaves and needles, will result in "dirtier" chips with a greater percentage of bark and extraneous material. Technology is being developed to handle such material. Total tree chips will definitely increase in volume.

5. Greater use of building waste and recycled fiber will continue but at a slower rate than for the past decade. All kinds of woods waste will be more heavily used as an energy source in the future.

6. The potential for growing cellulose in the Tropics and Subtropics is great, and activities in these areas, such as in South America, are rapidly expanding. Wood from plantations will be from pines or eucalypts, often grown for very short rotations. These species, when grown as exotics, often have wood very different from that produced by older trees grown in their native range. Also to be used heavily in the future are mixed native tropical hardwoods which, with their wide mixture of species with many differing wood qualities, create major problems for the pulp manufacturer.

47

INTRODUCTION

No matter what we may wish or do, the quality and type of wood available to the pulp industry in the future will be different from the past. Although the supply and demand for timber now appear to be in balance, projected demands for forest products make it evident that production of the needed quantities of suitable wood at reasonable prices will become increasingly difficult. The greatly increasing demand for timber is not local, regional, or even national in scope; it is worldwide and must be looked upon as a global concern. This greater demand, along with more stringent economic and environmental restrictions, requires that timber be increasingly grown as a crop.

Today, large-scale efforts are being mustered to utilize more fully all available land and timber. It is reported that, with full utilization, 50% more fiber can be obtained from each acre [1]. I feel this figure is too conservative, especially when full use is made of all silvicultural and utilization tools now available. Wood residues, once considered waste, are now finding increasingly widespread use. Such residues, both from manufacturing and forest harvest, have wood qualities considerably different from the current roundwood from mature trees. Use of residues formerly wasted, and the quality of wood and paper made therefrom, is very important.

Recent environmental pressures have restricted the scope of timber production in some areas and have increased the need to grow more timber on each acre available. Coupled with this concern, the increased cost of forest and mill operations and a need to liquidate the planting investment as soon as possible have resulted in the harvesting of timber at ever younger ages. This is causing a major shift in the type of wood available to the forest industries.

To further complicate matters, there are additional demands for available cellulose which are causing concern to the forest industry. As oil and coal become more expensive and difficult to obtain, the renewable resource, wood, is being increasingly viewed as a useful source of energy. Many forest industries have the objective of becoming "energy self-sufficient" by using all available residues; however, to achieve this goal, they will also need to use some material otherwise suitable for pulping. According to Smith [2], who calculated the needs and costs of wood as an energy source for pulp mills in the South, a 2000 ton per day mill that obtains all its energy from wood, will require about 40 % more land than will be needed (at today's productivity) to satisfy the wood requirements for the manufacture of paper. It is evident that the demand for wood and wood residues as a source of energy will increase even if mills do not rely solely upon them for energy production.

Other possible uses of cellulose are for the production of chemical products, such as sugars, plastics, and petroleum substitutes [3]. The extent of the demand for chemical usage will depend on the price of oil and coal; even now there are some products that can be made more cheaply from cellulose than from petroleum. New methods of quick and inexpensive production of simple sugars from wood are now under pilot plant test.

What will be the impact of the heavy demand for wood to make paper, boards, chemical products, and energy, as well as the increasing use of forest land for other than timber production? It will most certainly mean an intensification of forest management which will result in a change in the quality of wood available

to the pulp industry. It is mandatory that the changes in wood be recognized and that, as these changes take place, the industry have available the methodology to adapt to this differing raw material.

Chances to increase productivity are great; the wood harvest annually in the South as reported by the Southern Forest Institute [4] is only one-fifth to one-fourth of the biomass produced each year. Additionally, growth on the bulk of the southern forest land is only a fraction of the potential if good management, fertilization, and genetically improved trees were used.

It is the objective of this paper to review a few of the reasons why wood quality will change and how this may affect the pulp industry. Many supporting data are available to indicate what the changes will be, but only a few can be cited here.

WOOD AGE

It is certain that trees available to the pulp mills in the future will be smaller and younger with a higher proportion of juvenile wood than timber currently used. This phenomenon will be of much greater importance for conifers than for hardwoods because most conifers have larger differences in wood quality between juvenile and mature wood than do the hardwoods. As forest management becomes more intensive in the attempt to produce more wood on each acre, thinning will be extensively practiced in young plantations, resulting in a high proportion of juvenile wood. Rotation ages will be reduced in an attempt to optimize the economic returns from forest production, especially if volume is the criterion of production rather than weight of dry wood. In addition to the harvest of younger trees, much greater use will be made of heretofore unmerchantable tops and plywood cores, both of which are essentially all juvenile wood.

Differences in wood between young and older trees are illustrated for 11-year-old and mature loblolly pine in Table I. Note the higher gravity, longer cells, and thicker cell walls in wood from mature trees.

To illustrate further how some wood and pulp characteristics vary with age and kind of wood, a portion of a table from Semke and Corbi [6] is summarized in Table II. Trends shown are typical for juvenile and top wood compared to mature or older wood. In addition to the characteristics indicated, print uniformity was

TABLE I
Wood Qualities of 11-year-old Loblolly Pines Compared to 30-year old Trees[a]

Wood Property	11-year-old trees (juvenile)	30-year-old trees (mature)
Specific Gravity	0.42	0.48
Density (lbs./cu.ft.)	26.2	30.0
Tracheid length (mm)	2.98	4.28
Cell wall thickness (microns)	3.88	8.04
Lumen size (microns)	42.25	32.78
Cell diameter (microns)	50.01	48.86

[a] Adapted from Zobel and Kellison [5].

TABLE II
Wood and Paper Properties from Several Different Types and Ages of Loblolly Pine Wood[a]

Source of Fiber	Average Fiber Dimensions			Average Sheet Properties		
	Length (mm)	Width (microns)	Wall Thickness (microns)	Sheet Density (gm/cc)	Tear (gm/cm/5cm)	Tensile (lb/in)
Sawmill Chips	2.80	46.7	5.3	0.536	58.2	21.7
Conventional Roundwood	2.48	44.1	4.8	0.562	57.2	24.9
Topwood	2.43	42.1	4.4	0.572	48.7	26.9
15-year-old Trees	1.86	42.1	4.0	0.590	45.3	26.5
10-year-old Trees	1.62	40.9	3.4	0.613	46.5	26.6

[a] Adapted from Semke and Corbi [6].

much better for the young trees and topwood than for sawmill chips or conventional roundwood.

The impact of the wood qualities of young pine has recently been evident in some mills that have used large volumes of soil bank timber under 15 years of age. Yields per unit volume or unit green weight have dropped from 5 to 15% and the paper produced has qualities that differ from the usual kraft paper. Young pine has lower wood density, higher moisture content, shorter cells with thinner walls, a higher hemicellulose content, and less tall oil yield than does mature pine; paper produced therefrom will have higher burst values and sheet density with good printability but weaker tear properties than that produced from older wood. A study of 12-year-old loblolly pine [7] determined that the manufacturing cost of one ton of pulp from juvenile wood is about 65% more than the cost of one ton of pulp from mature wood. Much of this differential is due to increased cost of harvesting small trees, but about 10% was caused by the lower wood specific gravity, resulting in a reduction of mill capacity to 91% of that achieved when mature wood is pulped.

The effect of young hardwoods on wood and paper properties is less than for young pine. In their summary, Jett and Zobel [8] reported yields from young hardwoods were somewhat lower than from older trees, and burst of paper made from juvenile wood was slightly superior and tear slightly inferior to that made from mature wood. In general, the biggest drawback to the use of young hardwoods is the inclusion of bark (and often the limbs and leaves), which results in lower yields of dirty pulp that often has drainage problems and is difficult to bleach.

The differences in wood properties between juvenile and mature wood and the pulp and paper properties of three species, 25 years of age, are shown in Table III [9]. Fiber length differences between juvenile and mature wood are considerable for all three species, while other cell characteristics are rather similar. Moisture

TABLE III
Wood Characteristics of Three Hardwood Species—Breast Height Values[a]

By Age Segment	Sweetgum	Sycamore	Ash
Specific Gravity			
Rings 1 - 10	.49	.46	.54
Rings 10+	.50	.49	.54
Fiber Length (mm)			
Ring 1	1.33	1.38	0.79
Ring 3	1.51	1.60	0.90
Ring 10	1.90	1.87	1.18
Ring 25	1.87	1.84	1.14
Cell Diameter (microns)			
Ring 10	27.15	24.78	20.77
Ring 25	29.35	26.03	22.73
Lumen Width (microns)			
Ring 10	12.22	12.95	13.75
Ring 25	12.18	11.38	14.90
Wall Thickness (microns)			
Ring 10	7.46	5.97	3.55
Ring 25	8.66	7.38	3.94
Length-Width Ratio of cells			
Ring 25	63.7	70.7	50.2
For Whole Tree			
Pulp Yield c/	48.4	47.1	44.9
Moisture Content b/	119.3	119.7	54.6
Brightness c/	26.0	28.0	33.0
Burst c/	57	73	60
Tear c/	125	147	132
Lbs. oven-dry pulp per ton of wood	407	412	539
Bark % by volume	10.0	5.5	7.5

[a] Adapted after [9].
[b] Based on dry wood.
[c] When pulped under identical conditions of 90 min. cooking, 20% active alkali, 4:1 liquor to oven-dry wood ratio, temperature 344° F (110 p.s.i.).

contents and yield differences among the three species are large, indicating that species differences are of considerable importance.

For young hardwood trees 9 to 13 years of age, Barker [10] found similar among-species differences except for gum and sycamore; also he reported no important differences between young and mature wood of these species. He found fibers of mature oak beat faster than young oak but that generally young wood of the hardwood species tested should present no penalties in pulping and papermaking when compared to mature wood.

SPECIES MIXTURE

With shortened rotations and more complete utilization, the species mixture available to the mills will change. In the South, many mixed hardwood stands that are now being harvested are being replaced by pine plantations with little mixed merchantable hardwood. Under current economic and land use pressures, and forest management practices, the proportion of pine available to the mills in the South will increase greatly in the next few years while the hardwood supply will decline. Under current hardwood management methods the faster growing "soft" hardwoods such as sweetgum and sycamore are favored while the "hard" hardwoods like oaks and hickories generally receive minimal management. Thus the current high proportion of "hard" hardwoods will decline as greater acreages in the South come under intensive forest management.

In the Lakes States and the Northeast, a very large volume of hardwood, mostly aspen, is becoming more generally available. This vast reserve of cellulose, now only partially utilized, will become of greater importance to the pulp industry unless much of the area is tied up by environmental restraints. Certainly, greater efforts to utilize more fully this kind of wood are in order.

There is a vast inventory of hardwoods available in the Tropics. However, inventory figures about timber available from these forests, made up of many species with greatly differing woods, are deceiving. In some areas much of the inventory cannot now be economically extracted and difficulties are generally encountered in regenerating these biologically complex forest types. On a relatively small scale, plantations of tropical conifers and hardwoods are being established but this effort is expensive and the biological problems are many. The wood of many tropical hardwood species contains phenolic substances in the heartwood, and silica deposits hard to handle in pulping. Pulping a mixture of diverse species with such varied qualities is difficult but can be done [11]. Gomez and Mondragon report that they successfully pulped more than 100 species of tropical hardwoods in Colombia and can increase their current 40% of the furnish using this material to 80%. Vast quantities of tropical hardwood will be available and must be used, even though the final product may be marginal under present standards for paper on the world market. Mill chemists and pulping specialists have a real challenge ahead to adjust to the conglomerate wood mixtures from tropical hardwoods, but such must and will be done.

Much of the best timber that will become available from the tropical and subtropical areas will be from exotic pines and certain exotic hardwoods such as Eucalyptus and Gmelina. In the warm, humid climates, growth is exceedingly rapid and most species will be harvested while the trees contain only juvenile wood. The resulting raw material will thus be quite different from the mature wood obtained from the native range of the species involved. Although most species being planted have very desirable wood in their native range, some will produce completely different wood in the new, exotic environment; sometimes this wood is or marginal value for paper manufacture. In some ways short rotations can be beneficial; for example, the undesired phenolic substances in mature eucalypt wood will be avoided if the trees are harvested at a young age.

GENETICALLY IMPROVED WOOD

A major objective of most forest tree breeding programs is to develop wood most desirable for the products manufactured by the industry concerned; the most important characteristic is wood density or specific gravity. Whether high or low specific gravity is desired, one major result of the breeding program for wood quality will be to produce a more uniform wood. Trees harvested will all be of the same age and of similar size grown in plantations; the effect of similar growth conditions plus the uniformity obtained by breeding a specific type of wood will result in a much more homogeneous raw material than is now available from natural forest stands.

Breeding programs result in trees with straighter stems and smaller limbs which reduces the percentage of undesirable reaction wood. Differences in the pulp and paper resulting from better formed trees are of real value [12]. It was found that straight, small-limbed trees had better pulp yields than did average trees and the pulp quality was improved.

Of special interest is the development of trees for special woods or for increasing the specific gravity of juvenile wood for short pine rotation. Results from breeding for high density juvenile wood are very promising [13] and indicate the feasibility of developing strains of loblolly pine with high juvenile wood specific gravity along with rapid growth. An increase of 2–4 lb/ft^3 is possible in 10-year-old trees by choosing high gravity parents. Generally it will be possible to develop trees with desired wood with a relatively small effort in addition to the normal breeding program. The greater uniformity and changed qualities of such wood must be adjusted to by the papermaker.

TOTAL-TREE CHIPPING AND WASTE CELLULOSE

It is necessary to emphasize that the wood from total-tree chipping is different from that of the merchantable bole. There is a high proportion of bark (up to 14%) with considerable dirt and debris associated with bark, needles and leaves. Such dirty chips were at one time considered unusable for most papers but are now accepted, although sometimes reluctantly, by mill personnel as a part of the furnish for bleached as well as unbleached papers. Because limbs are chipped there is a high proportion of reaction and juvenile wood with short fibers, and varying cellulose contents. All factors make for a different kind of wood that the industry must determine how to use to best advantage on an increasing scale.

Along with the total-tree chips, tops from standard logging operations are being more widely used. These often also produce dirty chips with problems similar to those of total-tree chips. When pulped under comparable conditions, Semke and Corbi [6] found that debarked topwood (from a 4-in. to 2-in. top diam) had wood fiber properties and paper properties intermediate between young pine and conventional roundwood. If in the future stumps become used in quantity, still another type of "dirty" wood will be available with its own unique problems of utilization. Add to this the increased use of recycled fibers from paper and building waste, and the pulp manufacturer indeed has challenges if he is to maintain desired yield and current quality standards.

THE FUTURE

Because of the renewability of the forest resource, the high prices and future scarcity of petroleum and the environmental difficulties related to the use of coal, it is evident that wood production will need to be increased to supply the pulp and paper industry, the solid wood products companies, more use of wood for energy, and perhaps even use of cellulose for chemical products. Increased wood production will require more intensive forest management, higher prices for timber and shorter rotation lengths [14]. It will mean a change in species availability and much wider use of what are now considered undesirable chips for pulp production.

Other than its effect on the total amount of cellulose, how will the changes in form of wood affect the industry? In the short term it will mean a change in methodology and revised product and quality standards. Some persons have told me that in the long term, the characteristics of the fibers and their form will not be of great importance. They argue that industry is looking to the time when the main usage of cellulose will not be in a fiber form as produced in the tree but as reconstituted cellulose and lignin products in which fiber identity has been lost. Products will be made to the desired size and form with suitable strength, fire-resistant and water-resistant properties, much as the present day chipboard, hardboard, and flakeboard can be tailor-made for different end uses. I feel that this is an accurate assessment, and that the needs in the future will not be dependent on fiber length, wall thickness, or cell size, but more on the useful chemical constituents of wood. If timber is reduced to the form of reconstituted cellulose, large amounts of energy will be required; therefore the speed with which such conversion takes place will be dependent on the cost and abundance of energy available as well as on the timber supply. One of the brightest spots of all is that the timber supply is renewable and the industry can be largely self-supporting in energy requirements, using a high proportion of waste, and still be within limits of environmentally acceptable methods.

REFERENCES

[1] K. E. Lowe, *Pulp and Paper,* 47, 42 (1973).
[2] H. D. Smith, "Wood as an energy source for the southern pulp and paper industry," presented to members of the N. C. State Tree Improvement Cooperative 1974.
[3] I. S. Goldstein, "The potential for converting wood into plastics and polymers or into chemicals for the production of these materials," to be presented to the 169th Ann. Meet. of the American Chemical Society, Apr. 6–11, 1975.
[4] Anon., Southern Forest Institute forestry facts, 1972.
[5] B. J. Zobel and R. C. Kellison *Tappi,* 55, 1205 (1972).
[6] L. K. Semke and J. C. Corbi "Sources of less coarse pine fiber for southern bleached printing papers," Proc., 1974 Ann. Meet., TAPPI, Miami, Florida, 1974, pp. 295–304.
[7] D. G., Kirk, L. G. Breemen, and B. J. Zobel *Tappi,* 55, 1600 (1972).
[8] J. B. Jett and B. J. Zobel "Wood and pulping properties of young hardwoods," *Tappi* (in press).
[9] R. L., McElwee, R. C. Tobias, and A. H. Gregory *Tappi,* 53, 1882 (1970).
[10] R. G. Barker, "Papermaking properties of young hardwoods," *Tappi* (in press).
[11] C. H. Gomez and I. Mondragon "The pulping of Colombian hardwoods for linerboard," *Tappi* (in press).
[12] R. L. Blair, B. J. Zobel, E. C. Franklin, A. C. Djerf, and J. M. Mendel, *Tappi, 57,* 46 (1974).
[13] D. I. Matziris and B. J. Zobel *Sil. Gen.,* 22, 38 (1973).
[14] B. J. Zobel, "Increasing productivity of forest lands through better trees," S. J. Hall Lectureship, Univ. of Calif., Apr. 18, 1974.

EARLY EXPERIENCES FROM THE SWEDISH WOOD-BASED CHEMICAL INDUSTRY

INGVAR JULLANDER

Swedish Forest Products Research Laboratory,
Box 5604, S-114 86,
Stockholm 5, Sweden

SYNOPSIS

During and a few years after the Second World War, an important chemical industry was built up in Sweden based on wood as raw material together with sodium chloride and electric power. An astonishingly large variety of simple chemical products was produced, many of them vital to the Swedish society. The main intermediary product was ethanol obtained from sulfite waste liquor through fermentation. Glycol products were made via ethylene and ethylene oxide. Oxidation to acetaldehyde, followed by aldol condensation, and to acetic acid gave products such as butanol, butyl acetate and octanol. The manufacture of a cellulose ether, ethyl-hydroxyethyl cellulose provides a good example of a well integrated system.

INTRODUCTION

A combination of good luck and able political leadership made it possible for Sweden to pass the years of the Second World War in peace. But it was a period of utter isolation. Normal trade relations were at times almost totally cut off, especially towards the west. After peace was restored in 1945 the shortage of chemicals remained for a number of years. The chemical industry that eventually developed was built on three foundations: an ample supply of wood, the availability of cheap hydro-electric power and sufficient supply of sodium chloride.

Wood was used in three ways for the production of chemicals. First, wood distillation in connection with charcoal manufacture gave us methanol, acetic acid, acetone, and wood tar. Second, from the kraft pulping process we obtained naval stores: turpentine and tall oil. Wood distillation was never of great importance and the process was discontinued very soon after the end of the war. Naval stores, as a by-product of kraft pulp manufacture were, on the other hand, able to withstand all attacks from the petroleum-based industries and are today very much in demand, not the least in the U.S.

55

I shall concentrate, however, on chemicals based on sulfite waste liquor. An astonishingly large variety of uncomplicated products were produced, many of them vital to our daily life. The main intermediary product was ethanol, obtained from dissolved hexoses in the sulfite waste liquor through fermentation by the fungus *Saccharomyces cerevisiae*. A small amount of methanol was obtained at the same time, about 5% of the ethanol production.

By far the largest part of the pioneering research and development work was done by Mo och Domsjö AB in northern Sweden, and the chemical industry subsequently built up was established in Örnsköldsvik on the coast of the Gulf of Bothnia. It was integrated with an existing sulfite mill specializing in the production of dissolving pulp and with an existing chlorine plant. In this pulping process the polysaccharides of the wood are broken down to a higher degree than in ordinary paper grade pulp manufacture. This naturally increases the yield of hexoses and consequently also that of ethanol in the waste liquor. As a matter of curiosity it may be added that during two consecutive summers in the middle of the war the crop of hay was severely diminished because of unusually low rainfall. The pulp industry was called upon to produce a highly degraded type of pulp edible for cows and horses and suitable as a partial substitute for hay. This created ideal conditions for obtaining ethanol in high yield. Altogether 640,000 tons of fodder pulp was made, a considerable quantity.

Normal yield of ethanol from the waste liquor is 140 l. 95% alcohol/ton dissolving pulp; paper grade pulp gives about half that figure, whereas the fodder pulp just mentioned could give 160–170 l. The production of ethanol through fermentation of sulfite waste liquor had long been practiced in Sweden. In fact, the first plant in the world for manufacture of ethanol from sulfite waste liquor started production in March 1909 at Skutskär in Sweden.

Just after the end of the war, 1946–47, there were 33 plants producing ethanol from wood. Maximum production was 60,000 tons/year calculated as 100% ethanol. Today only six of these plants are still active. As an intermediary product, the ethanol was used for the production of chemicals along three main lines which will be termed: the glycol line, the acetaldehyde line, and the cellulose ether line.
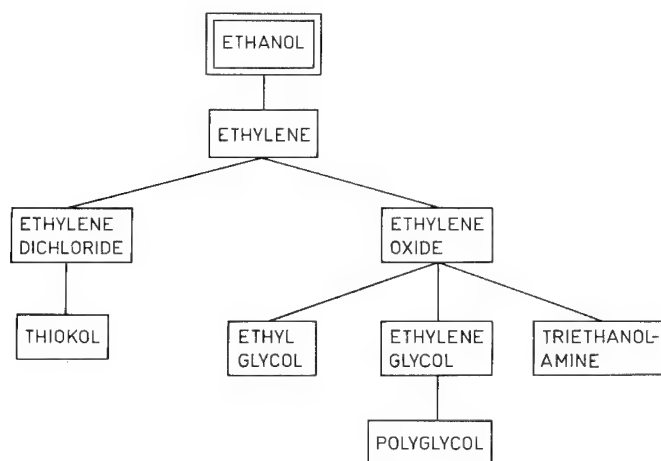

FIG. 1. The glycol line.

THE GLYCOL LINE (Fig. 1)

Ethanol was dehydrated to ethylene which in turn was converted to ethylene oxide. This may be astonishing news to those who have learned, on the contrary, that ethylene is a customary raw material for the production of ethanol. Ethylene chlorohydrin was an intermediary product, obtained through addition of hypochlorous acid. Later the production was modernized to a direct oxidation method, but at that time the ethylene was based on petroleum. The ethylene oxide then served as starting point for a large number of products.

Reaction with water gives ordinary ethylene glycol, used as an antifreeze agent in automobiles, but also needed as raw material in the manufacture of explosives. Glycerine was of course in short supply and nitroglycol was used as substitute for nitroglycerin. Sulfur was available as sulfide ore within the country and nitric acid was available via an ammonia plant. This safeguarded the nitration process and an important part of the explosives industry—the manufacture of dynamite— was then safely based on indigeneous materials.

Ethylene oxide plus ethanol gives ethyl glycol, used in the paint industry and other industries. The corresponding reaction with ammonia gives triethanolamine which has many uses as an emulsifying agent and absorption liquor for gases in different industries.

It may be added that ethylene dichloride—obtained, of course, from the reaction of ethylene with chlorine—plus sulfur gave us thiokol, a kind of synthetic rubber useful for gaskets and similar items but characterized by a bad smell. This was a typical substitute material forced upon us by the circumstances. Production ceased almost immediately after the war. A series of polyglycols were also produced, and later production of nonionic surface active agents grew in importance. Today this is an important part of the Swedish chemical industry, not so much in tonnage as in quality—but it is no longer based on wood.

THE ACETALDEHYDE LINE (Fig. 2)

This line, in a way, is the most interesting and became quantitatively the dominating one. Ethanol was oxidized to acetaldehyde. By aldol condensation two molecules of acetaldehyde formed a new C—C bond and upon hydrogenation the
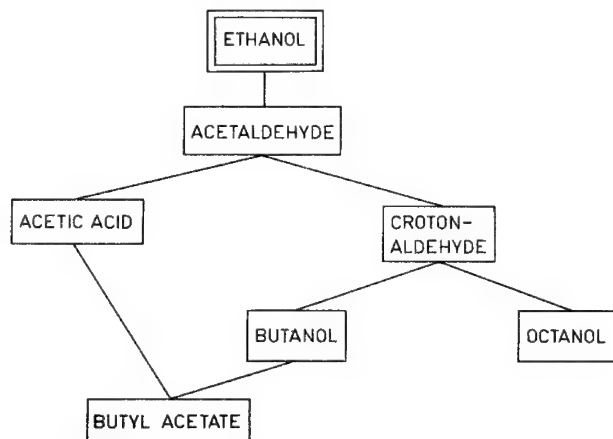

FIG. 2. The acetaldehyde line.

resulting crotonaldehyde gave butanol. Through repeated condensation octanol, or more precisely 2-ethylhexanol, was obtained instead. Another part of the acetaldehyde was further oxidized to acetic acid. In the beginning acetic acid was produced directly from ethanol through fermentation. This was a reliable technique but turned out to be uneconomical as by necessity the acetic acid was obtained highly diluted, at a concentration of about 10%, and the subsequent distillation was too costly.

The way was open to produce butyl and ethyl acetates and other acetic acid esters. This covered an essential part of the requirement of solvents for the paint and lacquer industry. The intermediary product crotonaldehyde found use as denaturant for ethanol.

Chlorine, alkali, and hydrogen needed for the reactions mentioned were all obtained through electrolysis of sodium chloride. The country had a sufficient supply of salt but could, if necessary, have produced it from sea water. Hydroelectric power was obtainable at all times without difficulty.

THE CELLULOSE ETHER LINE (Fig. 3)

This line is chosen here as an example of a well-integrated system. A double etherified cellulose, ethyl-hydroxyethyl cellulose, soluble in cold water, was produced from dissolving grade sulfite pulp. It has very much the same properties and uses as methyl cellulose. Etherification agents were ethyl chloride and ethylene oxide. Ethyl chloride was produced from ethanol plus hydrochloric acid gas, the latter obtained by burning chlorine and hydrogen together. Wood and sodium chloride therefore were the two basic raw materials. This simultaneous etherification introducing hydrophobic and hydrophilic groups in the cellulose chain, ethyl and hydroxyethyl, served the purpose of maintaining a balance in the solubility properties of the cellulose ether. It is insoluble in and consequently also washable by hot water but gives a clear aqueous solution at room temperature.
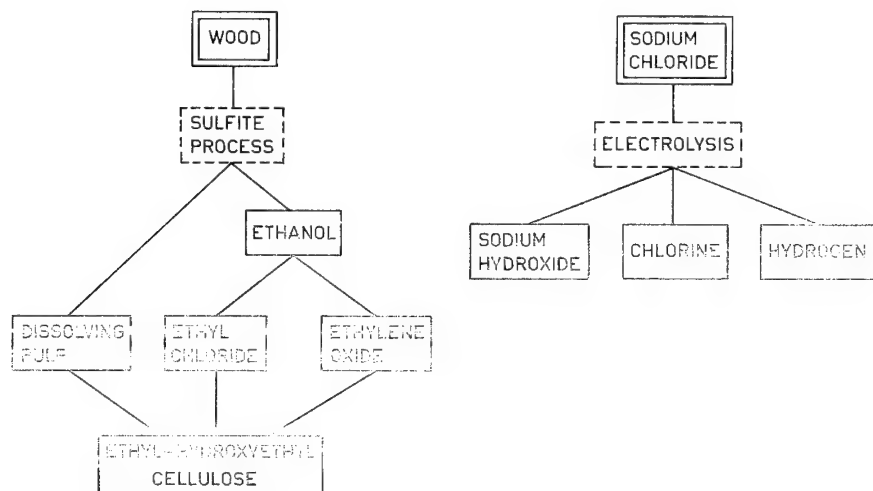

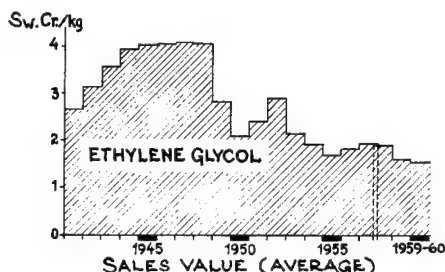FIG. 3. The cellulose ether line.

FIG. 4. Average sale value of ethylene glycol in Swedish crowns/kg. [From *Svensk Kemisk Tidskrift*, *74*, 140 (1962).]

In the beginning the production scale was very small for several reasons. Everything had to be started from scratch and the industry was asked to begin production of many different chemicals almost simultaneously. Also, during the war export was not possible and the production only had to cover our own needs. Selling was no problem and all prices were regulated by the government. On return to normal trade relations in the years after 1945, the number of chemicals produced was reduced drastically, and production of those remaining increased in order to gain competitiveness as a preparation for the international competition which was felt from about 1949 onwards.

Soon the supply of ethanol from sulfite waste liquor was insufficient, and the ethanol had to be bought from abroad, made from sugar beets, potatoes, or from molasses in sugar cane producing countries. This was an uncertain and unsteady market and eventually almost the whole industry became based on petroleum instead.

The development of prices during 1940–60 for two important products, ethylene glycol and butanol, is given in Figures 4 and 5. The annual production at the end of the war, 1946–47, amounted to about 1,200 tons of glycol products and 1,100 tons of products belonging to the acetaldehyde line. In 1960 the last figure was 18 times higher, but by that time production was no longer based entirely on wood as basic raw material. The average sale price from Sweden, in 1974, was around 3.50 Sw cr/kg for ethylene glycol and 3.00 Sw cr/kg for butanol. It should be added that water-free, so called absolute, alcohol was also used in considerable quantities as fuel for automobiles. A mixture of ethanol and gasoline (25:75), "bentyl," was indeed used for many years after the war.
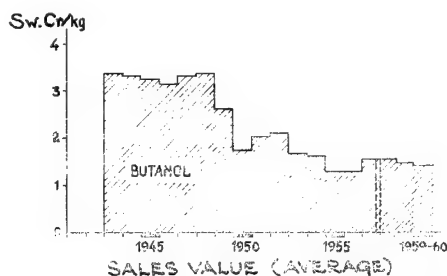

FIG. 5. Average sale value of butanol in Swedish crowns/kg. [From *Svensk Kemisk Tidskrift*, *74*, 140 (1962).]

CONCLUSION

In this historical review I have described developments which in a technical sense are not related to the forest products industry. The uses of ethanol as chemical raw material are technically in no way limited by the way it was produced. These developments were described with the express purpose of showing the far reaching importance of the availability of sulfite waste liquor in providing Sweden with necessary chemicals in a time of national distress.

It could be that when petroleum prices have risen substantially from today's level, the pulp and paper industry will be called upon to fill two needs: 1) to produce paper made from modified *wood* fibers, that is essentially mechanical pulp. It can be modified by thermal, chemical, or microbiological treatments but is still a pulp made with a yield close to 100%; and 2) to provide the chemical industry with wood as an essential raw material. This would include roots, stumps, and branches. Hydrolysis of the carbohydrates by chemical or enzymatic means to monosaccharides followed by fermentation is but one of many possible processes which might be adopted. Another route would give us aromatic chemicals by breaking down the lignin, perhaps by enzymatic methods.

THE FUTURE OF WOOD CELLULOSE IN TEXTILE AND PLASTICS APPLICATIONS

HERBERT L. HERGERT

ITT Rayonier Inc.,
605 Third Avenue,
New York, New York 10016

SYNOPSIS

The manufacture of man-made textile fibers, films, and plastics from wood cellulose has been a major, stable world-wide activity for a number of decades. Since wood cellulose is a renewable resource, it offers promise as a long-term raw material substitute for petroleum-derived fibers and plastics. For such replacement to take place, a massive investigative effort will have to be launched to develop new technology. Areas of research and development particularly needed are: (a) more economic, less capital-intensive processes for producing wood cellulose; (b) nonpolluting, lower labor processes for production of rayon fibers and films; (c) improved wet modulus fibers; (d) simplified esterification methods; and (e) an improved understanding of the physics and chemistry of cellulose. Although the utilization of pulping by-products, especially lignin, has offered a challenging field for investigation by the scientist, the real opportunity for meeting the challenge of petroleum lies in cellulose research. It will be interesting to see whether industry and academe in the western world will rise to meet this challenge.

INTRODUCTION

The decision by OPEC nations to restrict sales and substantially increase the price of crude oil during 1973–1974 rapidly translated into world-wide shortages of many organic chemicals used in the manufacture of plastics, films, and man-made fibers. This, in turn, belatedly focused public attention on the extremely limited nature of petroleum as a resource, a fact which ecologists, geologists, and others had been attempting to publicize for many years. Most of the developed nations, suddenly alarmed by the oil situation, have since launched various types of actions by which they hope eventually to regain energy and raw material independence. Prominent among these is the search for plastic and fiber raw materials not dependent upon oil. Wood scientists and technologists have taken heart from this turn of events because they had been carrying out investigations for years on

61

TABLE I
World [4] Man-Made Fiber Production[a] (Million lb)

Year	Rayon & Acetate	Non-Cellulosic
1966	7364	5227
1968	7780	7889
1970	7565	10351
1972	7833	13994
1973	8080	16727
1974	7700	16400

[a] Except acetate cigarette tow, olefin, and textile glass fiber.

ways to convert pulping by-products, forest residues, and bark into organic chemicals such as phenol, methanol, levulinic acid, etc., only to meet defeat by low priced petroleum.

Proposals for reconsideration of wood and bark as raw materials for conversion to organic chemicals are again beginning to appear in the literature, [1, 2] and research into the future challenge of wood chemicals is being stepped up. However, in our quest to establish the technology for conversion of wood to organic chemicals, we should not lose sight of the fact that the bulk of all organic chemicals manufactured in the developed nations are intermediates or additives for the production of polymers. Since wood constituents are primarily polymeric, it makes sense, at least from an energy and capital conservation point of view, to take advantage of this polymeric nature. Direct substitution should certainly have higher priority for research and development funding than development of techniques for breaking wood constituents into simple compounds which then must be reassembled into polymers.

The conversion of wood-derived chemical cellulose (also termed "dissolving pulp") into man-made textile fibers, transparent films, and thermoplastics has been a major stable world-wide activity for a number of decades. Cellulose is potentially available in adequate amounts to serve these end-uses for the long term because the trees or annual plants from which it is obtained require only the sun as their energy source. Furthermore, the end-products have a wide range of desirable properties. For example, man-made cellulosic textile fibers offer high moisture absorption, biodegradability and low oil requirement for manufacture [3]. Nevertheless, most of the growth in the plastics and man-made textile fibers industries during the last three decades has been based on crude oil or natural gas (see Table I) [4]. This is a dual consequence of oil which cost one cent per pound and a massive research and development effort by the North American and European chemical industry since World War II. Meanwhile, except in the Soviet sphere, cellulosic research has been virtually abandoned in industrial and university laboratories alike. If petrochemical based products are to be even partially replaced in the future by those based on cellulose, a major investigative effort will have to be launched to develop new technology. It is the intent of this paper to identify areas of research and development which are particularly needed.

PROCESSES FOR CHEMICAL CELLULOSE MANUFACTURE

A brief overview of the processes currently used for chemical cellulose manufacture will provide needed background in identifying research and development needs. Two major sources of base raw material are used, cotton linters and wood. Other types of vegetable materials could undoubtedly be used, e.g. straw, reeds, sugar cane bagasse, kenaf, jute, etc., but the cellulose-isolation (pulping) procedures from these materials have not so far resulted in material usable in commercial viscose, esterification or etherification processes. Since the forest offers the largest, still untapped source for future growth in chemical cellulose supply, and since it does not require the type of land needed for the world's expanding food needs, emphasis will be placed on wood cellulose.

Two major types of pulping are used to produce chemical cellulose from wood; both involve an acidic first stage to depolymerize and remove hemicellulose (non-cellulosic carbohydrate polymers, primarily glucuron-xylan and glucomannans) and an alkaline second stage for delignification and/or further hemicellulose removal. Bleaching for whitening purposes and depolymerization to a precise intrinsic viscosity level for enhanced reactivity are also features common to both processes. The prehydrolyzed kraft (PHK) process involves the pretreatment of wood chips in a pressure vessel with water, dilute acid, and/or steam at temperatures ranging from 155 to 180°C followed by cooking with "kraft" liquor (a mixture of caustic soda and sodium sulfide). Washed pulp is then bleached in multiple stages with chlorine, sodium hypochlorite, dilute caustic soda, and chlorine dioxide, and extracted (optionally) with cold caustic soda or kraft white liquor under mercerizing conditions for further purification. The pulping spent liquor is combusted for heat and chemical recovery. Bleach plant effluent is submitted to secondary treatment for BOD reduction in aeration basins, or by air/oxygen activated sludge treatment. Usually only the highest purity chemical cellulose grades are made by this process since yields from wood are very low (28–33%). Higher yield chemical cellulose pulp could be made under less severe prehydrolysis conditions, but it would not have nearly as good reactivity as pulp at the same yield level made by the sulfite process.

Acid bisulfite dissolving pulp is produced by cooking wood chips in an aqueous solution of sulfur dioxide and sodium, ammonium, or magnesium bisulfite under conditions somewhat more strenuous, i.e. higher acidity, higher temperature and/or lower combined base level, than used to prepare normal sulfite paper pulp. The objective is to obtain low hemicellulose content and enhanced reactivity in the final product. Pulping is followed by a series of bleaching stages, one of which includes heating with caustic soda solution in a pressure vessel at temperatures ranging from 105–150°C. This stage is frequently referred to as hot caustic extraction (HCE). It generates a very high BOD load because it is used to remove the bulk of the remaining hemicellulose in the pulp by the classical carbohydrate alkaline peeling reaction. Spent liquor, as in the PHK process, is combusted for heat and chemical recovery. Effective means for secondary treatment of effluent from the bleach stages is currently a subject of intensive investigation. The Finnish Rauma process is a variation of the classical sulfite process in which chips are pulped in three stages in the same vessel. After impregnation with sodium bisulfite, cooking is conducted with sulfur dioxide and water, followed by hot sodium carbonate. In this case, the HCE stage effluent is, in effect, combined with that of the acid cook

TABLE II
Energy and Chemical Requirements for Chemical Cellulose Manufacture [5]
(Actual usage per lb product)

Wood, lb.	2.70 – 3.30
Caustic soda, lb.	0.10 – 0.22
Chlorine, lb.	0.07 – 0.09
Chlorine dioxide, lb.	0 – 0.01
Sulfur, lb.	0.04 – 0.17
Steam, lb.[a]	8.25 – 13.3
Electricity, KWH	0.30 – 0.52
Total energy in oil equivalents	0.8 – 1.2
Actual oil used, lb.	0.3 – 0.55

[a] Includes steam for liquor evaporation.

and both are combusted, resulting in a much lower bleach plant effluent disposal load.

Cotton linters are essentially unlignified, so preparation of chemical cellulose from them essentially involves mechanical cleaning, caustic cooking for xylan and wax removal, and mild bleaching for whitening and intrinsic viscosity reduction.

The chemical and energy requirements for chemical cellulose manufactured from wood [5] are shown in Table II. Rapid escalation in wood, chemical, and fuel costs were experienced during the last two years. Most mills still use fuel oil as part of their energy source, but it is quite possible to be entirely independent of oil usage (except for transport of the wood to the mill) by increased burning of wood and bark residues or coal. This decision is currently based on the economic trade-offs between the cost and use of oil in existing boilers versus capital required for substitute wood and bark-burning boilers and fuel-handling facilities. The relatively high caustic soda consumption is of particular concern because of the severe imbalance in caustic/chlorine usage potentially resulting from dislocations in the poly(vinyl chloride) industry. The latter has been a major consumer of chlorine, but this usage could rapidly decrease if PVC manufacturers cannot find economic means for reducing vinyl chloride emissions to the zero detectability level.

TABLE III
Effect of Bleached Bark on Viscose Filterability (Cellophane-Type System)

Wood Pulp, %	Bark, %	FN[a]
100	0	810
99	1	3620
98	2	5860
95	5	10600

[a] Filtration Number, 1000 is maximum acceptable.

TABLE IV
Effect of Wood Species in a Laboratory HWM Rayon System

Wood	U.S. Hardwood	Tropical Hardwood	
Species Selection?	No	Yes	No
Pulp, S_{18}, %	3.0	2.6	2.7
Rayon, Cond. Tenacity, g/d	5.0	4.1	2.7
Rayon, Wet Tenacity, g/d	3.2	2.5	1.5
Rayon, Conditioned Elongation, %	11.0	10.0	7.0
Rayon, Wet Modulus, g/d	0.78	0.65	0.40

The substitution of oxygen/alkali bleaching for part of the chlorine previously consumed in paper pulp bleaching will also contribute to this imbalance. A possible corrective may be available if current research on substitution of chlorine monoxide for chlorine dioxide in pulp bleaching is successful. Chlorine monoxide can be generated by the reaction of chlorine and sodium carbonate.

So far, little has been said regarding wood quality needed for chemical cellulose production. The use of whole-tree chipping followed by some type of crude separation of bark and wood has been widely touted as offering significant cost reduction and increases in yield of usable pulp wood chips per acre. The experimental results shown in Table III, wherein fully bleached hemlock inner bark was incrementally added to pulp prepared from bark-free hemlock wood and subsequently converted to viscose, shows that viscose filterability is unacceptable when only 1% bark is present in the wood furnish. Whole tree chips, even after several stages of refining contain levels of bark substantially higher than this, and therefore they are clearly unacceptable in wood pulp destined for viscose plants using today's technology.

Another type of problem is exemplified by the data [6] shown in Table IV. There is a vast supply of unutilized tropical hardwoods in parts of Central and South America, Africa, and Asia. The number of species per acre varies from 20 to 200, and the wood shows a wide variety of properties including density, pulping refractivity, and silica content. A random selection of 20 Indian hardwoods was pulped by the PHK process (most tropical hardwoods cannot be pulped by the acid bisulfite process) and converted to high wet modulus (HWM) rayon. Although the wood pulp chemical properties (D.P. distribution, alpha content, brightness, etc.) met the required specifications, the HWM rayon was noticeably deficient in physical properties. Even after careful species selection, the product properties were not as good as those attainable from the more homogeneous north temperate forest. Silica, phytosterol glucosides, calcium oxalate, triterpenes, and other minute particulate materials contained in the wood appear to be the major culprits.

Significant expansion of the chemical cellulose production industry will surely depend in part on successful research and development in the following areas:

1. An expanded economic raw material base. This will require (a) effective means for separation of bark and contaminants from whole tree chips, and (b) im-

TABLE V
Energy and Chemical Requirements for Rayon Staple

Component, lb.	Amount, lb.	Energy Req'd.[a] lb. of oil equivalent
Wood pulp	1.02	1.1
Caustic soda	0.90	0.37
Carbon disulfide	0.35	–
Sulfuric acid	1.35	–
Steam	17 – 30	1.1 – 1.8
Electricity, KWH	0.7 – 0.8	0.3

Total Oil Equiv. 2.8 lb./lb.

[a]Includes energy requirement for caustic soda manufacture, 1.04 KWhr per lb.

proved methods for particulate removal (silica, etc.) following pulping or bleaching.

2. Genetic tree strains higher in cellulose.

3. More efficient tree removal and transport methods.

4. Development of pulping processes for better product yield based on starting material. Approximately 25% of cellulose is currently lost in the preparation of high-alpha wood pulp.

5. Less capital-intensive pulp mills are needed to compete effectively with oil-based synthetics. Methods for achieving this should include (a) completely countercurrent bleaching to minimize water and heat use, (b) lower cost and more effective secondary treatment, and (c) reexamination of the national environmental priorities which have legislated zero-discharge facilities in the early 1980's. The cost-benefit ratio of removing the last 1–2% from effluents is highly questionable.

6. Profitable byproducts. The large sugar and isosaccharinic acid-containing waste streams from a chemical cellulose plant ought to be upgraded to a higher end-use than that of fuel. They offer ideal opportunities for fermentation to single cell protein, provided markets exist and lower cost and energy-consuming fermentation plants can be developed so that economics are favorable.

MAN-MADE CELLULOSIC FIBER

Rayon staple fiber offers major growth opportunities in the future for use in nonwovens and textile blends with cotton or polyester. Regular rayon is produced by slurry or sheet stepping a medium alpha pulp in 18% caustic soda solution, pressing out the excess alkali, shredding, aging (depolymerization), xanthation, dissolving in a sodium hydroxide solution, filtration, ripening (for redistribution of xanthate groups), deaeration, spinning into an acid bath containing zinc sulfate, chopping into staple length, finishing, and drying. High performance rayon is made by the use of high alpha pulp to minimize noncellulosic contaminants in the product and the use of regeneration retardants (HWM-type) or excess carbon di-

TABLE VI
Energy and Chemical Requirements for Polyester Staple

Component	Amount, lb.	Actual Oil Req'd.[a]	Energy Req'd. lb. of oil equiv.
Terphthalic acid	0.90	0.89	0.64
Ethylene glycol	0.38	0.39	0.35
Energy		–	0.33
		1.28	1.32

Total Oil Equiv. 2.60 lb./lb.

[a] Based on selected feedstock.

sulfide (polynosic-type) to obtain better cellulosic chain orientation and degree of crystallinity.

The energy and major chemical requirements for high performance rayon staple fiber are shown in Table V and compared with those of polyester staple manufactured by a continuous process from terphthalic acid and ethylene glycol (Table VI). The viscose process has a very high chemical requirement, including caustic soda which not only suffers from the caustic/chlorine imbalance mentioned previously but requires substantial amounts of energy (in the form of electricity) for its generation. Although oil is not required for rayon manufacture (coal or wood can be used as fuel), the high energy input required means that rayon cost and pricing is not independent of the factors affecting the cost of polyester.

Research needs can be divided into two categories, those for the existing viscose process and those for an ideal, new cellulose regeneration system. Briefly, these are:

1. For existing plants: (a) more effective emission controls—odor problems are very similar, though less intense than those experienced with kraft pulp mills; (b) lower caustic and energy consumption—Sihtola's double-steeping process is a good start in this direction; (c) improved rayon properties—better "cover" and wet modulus under regular rayon operating conditions would be desirable; and (d) elimination of the zinc requirement.

2. For new plants: (a) process tolerant of lower alpha pulp and/or pulp derived from bark-containing chips or wood species not desirable for paper manufacture; (b) no effluent, no sulfur process—DMSO/NO_2 [7], DMF/NO_2 [8] or DMSO/paraformaldehyde [9] may be a forerunner of the type of nonaqueous system needed; (c) dry spinning (if possible); (d) cellulose in the product should be higher D.P. than in rayon; and (e) low capital investment.

Man-made cellulosic fibers are, of course, also made by esterification to the triacetate or diacetate derivative. Pulp is pretreated with acetic acid or acetylated directly with an excess of acetic anhydride, acetic acid and a catalyst (usually sulfuric acid) to the triacetate stage and then saponified to the diacetate, precipitated, washed, dried, dissolved in acetone, filtered and "dry" spun. There are substantial research and development needs here, also, but the acetate producers seem to devote relatively greater effort to product and process improvement than those who manufacture rayon. For long-term expansion, it would be desirable to have a process for direct acetylation to the diacetate without generation of acetic acid by-

product. Stronger diacetate fiber with no shrinkage upon washing might expand usage in textiles (current market growth is mainly in filament tow for filtration), but there is considerable debate as to whether desirable aesthetics (elongation, softness, luxurious hand, etc.) can be retained.

CELLULOSIC FILM AND PLASTICS PRODUCTION

The total output of resins for plastic and film manufacture is substantially higher than that for man-made fibers (24.9 billion lbs in the United States versus 6.9, excluding cellulosics, in 1974). This is probably the greatest technological challenge facing cellulose in an effort to replace petrochemically-derived products, since the total usage in plastics is relatively small. Cellulose mixed ester plastics are the main contender, but they are relatively expensive compared to polyethylene, polypropylene, polyvinylchloride, and, even, polyester.

Regenerated cellulose for film (cellophane) continues to show growth world wide in spite of competition from noncellulosics. Most of the future growth can be anticipated in countries which have higher petrochemical costs than North America or Europe. On the other hand, discovery of a low cost, nonaqueous system for regenerating cellulose, previously mentioned in connection with fiber production, could change this situation because modern cellophane formulations have many desirable properties. Cellophane is made by the viscose process and differs from rayon fiber production primarily in the use of more "stressed" compositions, i.e., higher cellulose and lower caustic content in the viscose. Three primary research and development needs are: 1) means for reducing caustic soda and energy consumption; 2) improved, inexpensive emission and effluent control; and 3) development of wood pulp tolerant of a very "lean" viscose system, preferably by a process lower in cost than those used currently for cellophane pulp production.

Use of cellulose in plastics, other than as a filler or reinforcing agent, requires derivatization. Technically, the major problem is that cellulose is a crystalline solid, and all reactions involve two or more phases with very slow reaction rates. The net result is excessive byproduct formation. In the reaction of ethylene oxide with alkali cellulose to form hydroxyethylcellulose, for example, 35% or more of the applied ethylene oxide ends up as ethylene glycol or homopolymer which must be washed out of the product. Similar problems exist in the preparation of methyl, ethyl, propyl, and carboxymethyl ethers. Major research needs, therefore, include: 1) reactions with reduced byproduct formation; 2) homogeneous reaction conditions; 3) more efficient conversion to the intended product; and 4) nonaqueous systems for elimination of effluent.

CONCLUSION

A good future for the use of wood cellulose in man-made fibers, films, and plastics applications can be anticipated. It will require much increased recognition that this industry offers the opportunity for production of a widespread diversity of products with minimal dependence upon oil. Although the utilization of pulping byproducts, especially lignin, has offered a challenging field for investigation by the wood scientist, the real opportunity for meeting the challenge of petroleum lies

in cellulose research.   Based on the volume of cellulose-related research work now being reported out of the Soviet sphere, it appears that the message has been understood in the U.S.S.R.   It will be interesting to see whether industry and academe in the western world will rise to meet this challenge.   Finally, it should be emphasized that the cellulosic research and development that is undertaken must deal with the real issues and not be diverted by preoccupation with peripheral niceties.

Contribution No. 148 from the Research Laboratories of ITT Rayonier Inc.

REFERENCES

[1] W. H. M. Schweers, *Das Papier, 29,* 1 (1975).

[2] I. S. Goldstein, in "Renewable Resources for Plastics," pp. 25–43, A.C.S. Div. of Chem. Marketing and Economics, 1975; cf. *Chem. Eng. News, 4* (May 26, 1975).

[3] T. E. Muller, D. G. Unrau, and L. L. Nejelski, "The New Rayons," paper presented at 33rd Annual Technical Conference of Soc. Plastic Engineers, May 5–8, 1975, Atlanta, Georgia.

[4] *Textile Organon, 46,* 1 (1975); Data presumably excludes production in the Soviet sphere.

[5] Data are derived from 1974 operating records of dissolving pulp mills in the United States and Canada.

[6] H. L. Hergert, T. E. Muller, and S. E. Church, Chemical Cellulose for High Performance Rayon, TAPPI 1973 Dissolving Pulps Conference Preprints, pp. 135–138, Oct. 1973.

[7] H. L. Hergert and P. N. Zopolis, Can. Patent 786,225 (1968).

[8] L. P. Clermont, Can. Patent 899,559 (1972); R. G. Schweiger, *Chem. Ind.,* 296 (1969).

[9] D. C. Johnson, M. D. Nicholson and F. A. High, Dimethyl Sulfoxide-Paraformaldehyde—A Nondegrading Solvent for Cellulose, paper presented at Eighth Cellulose Conference, May 19–23, 1975, Syracuse, N.Y.

PLASTICS FROM WOOD

RUDOLPH D. DEANIN

Plastics Department,
Lowell Technological Institute,
Lowell, Massachusetts 01854

SYNOPSIS

Commercial uses of wood in the plastics industry include: 1) plywood, wood waste, and impregnated wood using small to moderate additions of synthetic resins; 2) wood flour reinforcement in phenolic molding powders; 3) cellulose as continuous matrix in viscose rayon, cellophane, and vulcanized fiber, and 4) as reinforcing fiber in high-pressure laminates and in amino resin molding powders; 5) thermoplastics based on cellulose esters and ethers; 6) semi-commercial use of lignin as a reinforcement in rubber and an extender in phenolic resins; 7) other polymers from trees including natural rubber, gutta percha, terpenes, and miscellaneous resins; and 8) potential use of fermentation, pyrolysis, and coking as starting points for synthesis of conventional raw materials for the plastics industry. Development of these commercial processes, and a variety of advanced research projects, are recommended to hasten the day when the continued growth of our polymer industries can be based on a sound continuing supply of renewable raw materials from our forest products industries.

INTRODUCTION

Wood has been used in plastics ever since the plastics industry began. During the past 30 years, petroleum has offered more available, lower-cost raw materials for plastics, but our supply of petroleum has been depleted before the plastics industry even entered its major growth phase. Thus it is imperative that we turn to more dependable, renewable raw materials such as wood, as a sound basis for continued growth of the plastics industry. As an effort in this direction, it is useful to review the proven commercial uses of wood in plastics, and also indicate some promising directions for future research and development.

WHOLE WOOD

Wood Products

Plywood and wood waste (chips and sawdust) are bonded by 5–10% of phenol-formaldehyde or urea-formaldehyde resin, to produce materials superior in many

71

ways to the original wood itself for use in building and furniture. This consumed 132,500 metric tons of phenolic resin for water- and weather-resistant applications, and 307,000 metric tons of urea- and melamine-formaldehyde resin for more decorative indoor applications in 1974 [1] and, of course, produced 10–20 times this amount of resin-bonded wood products.

Impregnated wood generally uses higher resin contents, such as 10–35% of phenolic resin, to increase the density, hardness, and durability of solid wood, and can thus be used to upgrade the quality of fast-growing low-cost woods.

Wood Flour

Phenolic molding powders were produced to the extent of 164,500 metric tons in 1974, mainly for use in electrical and electronic equipment, appliances and utensils. These molding powders are actually 50% phenol-formaldehyde resin plus 50% of filler, and the most common filler is wood flour. Thus, a major portion of our first and leading commercial thermosetting plastic is actually wood.

CELLULOSE

Continuous Matrix

The cellulose from wood is dissolved and reprecipitated to yield a variety of useful plastic products. Viscose rayon is a leading man-made fiber, particularly for use in tire cord. Cellophane was our first clear packaging film, and remains one of our best. Less well-known is the so-called "vulcanized fiber," a tough plastic sheet made by swelling cellulose with aqueous zinc chloride, forming and shaping the gel, and leaching out the zinc chloride to leave a hard, tough, flame-, electrical-, and chemical-resistant sheet which finds varied uses in electrical and other industries. In all of these, cellulose serves as the continuous matrix in the plastic product.

Reinforcing Fiber

High-pressure laminates are made by impregnating paper with phenol-formaldehyde or melamine-formaldehyde A-stage resins in aqueous and/or alcoholic solution, drying the impregnated paper, stacking it in layers, and curing it in a hot press. This consumed 50,100 metric tons of phenolic resin and 21,000 metric tons of melamine resin in 1974. For decorative laminates in building and furniture, the phenolic resin generally serves as a structural base while the light-colored melamine resin serves as a decorative and protective top layer. The other major field of use is electronics, particularly as printed-circuit boards.

Urea and melamine molding powders offer better color than phenolics, and therefore use cellulose fibers instead of wood flour to preserve their light, bright colors. Urea-formaldehyde-cellulose molding powders were produced to the extent of 21,800 metric tons in 1974, mainly for electrical fittings and bottle caps. Melamine-formaldehyde-cellulose molding powders amounted to 19,500 metric

tons, mainly for dinnerware. In both these resins, cellulose was actually a major portion of the total plastic product.

Cellulose Derivatives

The term "cellulosic plastics" generally applies primarily to cellulose acetate, along with the co-esters cellulose acetate-propionate and cellulose acetate-butyrate and a smaller amount of ethyl cellulose ether, most often plasticized by phthalate or phosphate esters. These are high-quality, consumer-appealing thermoplastics of high clarity and gloss. Production in 1974 was 75,600 metric tons, used primarily in packaging, personal products (tools, brushes, pens), industrial protective sheeting, eyeglass frames, and automotive decorative parts. As the petroleum-based commodity thermoplastics become more expensive, we should expect to see larger utilization of these attractive cellulosic plastics.

LIGNIN

The lignin extracted from wood in papermaking appears to have a number of potential applications in the polymer industries, although none of these has found solid commercial success. The leading candidate is probably reinforcement of rubber, where lignin is comparable with carbon black, for improving the properties of rubber products such as tires. Another likely possibility is the use of lignin phenolic structures in place of phenol in phenolic resins; the lignin types which have been used thus far have acted primarily as moderate extenders, but new modifications might hopefully perform more like phenol itself in such products. Extension of epoxies and polyurethanes has also been reported, but not developed commercially. Conversion of lignin into methanol and phenols has also been considered as a source of basic "petrochemical" raw materials for plastics; the primary question here will be process yield and economics.

OTHER POLYMERS FROM TREES

The rubber tree, *Hevea brasiliensis,* gives us an excellent elastomer which, unlike petroleum-based elastomers, is completely renewable. Continuing research is steadily improving both the economics and the quality of the product. Many chemical derivatives also form useful plastics [2].

Related species produce trans-polyisoprene which has proved directly useful in plastics. Gutta percha is a hard, tough plastic used in undersea cable insulation and golf ball covers. Balata is a blend of trans-polyisoprene with hydrocarbon resins, which has been used for machinery belting, and chicle is a blend of cis- and trans-polyisoprenes with hydrocarbon resins, which has been used as the base for chewing gum.

Terpenes from pine stumps have found a variety of uses, in natural and modified forms, as modifying additives in rubber and plastics. Other natural resins such as amber, rosins, and copal are also derived from certain species of trees and found useful in formulating polymeric products, particularly moldings, coatings, and adhesives [3,4].

FERMENTATION AND PYROLYSIS

There are a growing number of studies showing that whole wood, cellulose, or the hemicellulose byproducts of papermaking, can be converted chemically or biochemically into conventional basic "petrochemical" raw materials for plastics [5]. Wood can be pyrolyzed to $CO + H_2$ and then converted to methanol, ethylene, acetylene, propylene, benzene, and toluene. Wood can also be reacted with CO under heat and pressure to produce hydrocarbon oils which can then be cracked like petroleum to produce olefins. Cellulose can be hydrolyzed to glucose, then fermented to ethanol, which is converted to ethylene and butadiene. Xylan is hydrolyzed to xylose, converted to furfural, and on to tetrahydrofurane, and its derivatives, for polyethers, polyesters, polyurethanes, and polyamides. All together, these processes permit us to synthesize practically all of the polymers, polymer chemicals, and plastics currently made from petroleum. They are not yet competitive economically, but dwindling petroleum supplies and accelerated research on wood conversion processes could make them serviceable and competitive in a few more years.

COKE

Before the advent of the petroleum-based organic chemical industry, coke from coal was the starting point for synthesis of calcium carbide, acetylene, chloroprene, vinyl chloride, vinyl acetate, acrylic esters, acrylonitrile, melamine, and a host of other basic chemicals and monomers for the plastics industry [6]. Coke from wood could presumably be the starting point for the same family of chemicals. Probably coal will remain the more economical as long as reasonable supplies of coal remain, while wood will take over after that.

SUGGESTIONS FOR FUTURE RESEARCH

1. *Wood Slurry Processing.* If trees can be ground in the forest, slurried in water, and piped directly to processing plants, materials handling would finally approach the facility of the petrochemical industries. The aqueous slurry of ground wood would also provide a new raw material of low cost and high potential quality for plastics processing. Addition of aqueous binder resin and centrifugal removal of water could produce both simple and complex shapes, needing only pressure and heat to recreate wood-like or super-wood products in a great variety of forms, from building panels to highly sculptured furniture. This could conceivably replace many of the present plastics processes and products. Such a development would require not only good wood and polymer chemists, but even more inventive process engineers.

2. *High-Pressure Laminates.* Melamine-surfaced decorative laminates are already popular in quality use in building and furniture. If rigid vinyl and reinforced polyester panels become uneconomical due to their petrochemical parentage, such high-pressure laminates could easily take their place in the growth of advanced modern design and construction concepts.

3. *Cellulose from Plants.* Cellulose is already available from a variety of plants, from primary high-quality products from cotton to secondary impure by-

products from sugar cane and other food crops. Increasing crop production of food may actually produce a simultaneous increase in byproduct cellulose such as bagasse. This might well deserve more intensive study to use it optimally in the plastics industries. High-yield cellulose crops such as kenaf may also offer us much greater productivity than forests for primary production of cellulose for plastics. These possibilities deserve increasing consideration in the present decade.

4. *Cellulosic Reinforcement of Synthetic Foams.* Wood flour and cellulose fibers convert weak, brittle phenolic and urea resins into strong tough plastics. Phenolic and urea foams are known, but they too are very weak and brittle. Perhaps the use of wood flour and cellulose fibers in these foams could make them strong, tough, and more useful. It should be noted that they already possess heat and chemical resistance superior to conventional foams, and that strength and toughness may be all they would need for commercial success.

5. *Waste Paper as Reinforcement for Plastics.* The largest portion of solid waste is paper, some of which is currently reclaimed. Chopped paper is sometimes used as an extremely efficient reinforcement for phenolic resins. Conceivably, waste paper, cleaned, treated, and chopped in various ways, could perform a wider variety of reinforcing functions, not only in phenolics, but also in amino and other plastics as well.

6. *Waste Paper for Fermentation or Pyrolysis.* Fermentation and pyrolysis routes from cellulose to basic chemicals for plastics were described earlier. Using raw cellulose from wood, these would thus compete with present uses of wood and paper. The same processes should work just as well on waste paper. Here they would not compete, but rather would help to reduce solid waste and to increase recycling of raw materials.

7. *Biodegradable Plastics.* To reduce solid waste accumulation, and to help close the ecocycle, biodegradable plastics would be superior to long-lived ones in solid waste. Use of cellulosic backbones, instead of petroleum hydrocarbon backbones, should certainly facilitate the problem of achieving biodegradability in plastics.

8. *Reinforced Cellulosic Thermoplastics.* Most of the current thermoplastics have been improved by addition of short-fiber reinforcement, particularly glass and asbestos. This has not yet been applied to the cellulosic thermoplastics. It might very possibly broaden their range of useful properties and applications.

9. *Cellulosic Thermoplastic Foams.* Cellulose acetate foam was commercialized briefly three decades ago. Since that time, most thermoplastics have been foamed, and several are extremely popular in foam form, but cellulosics have not been developed in this direction. With our modern foam technology, it is high time to reexamine the cellulose esters in such form.

10. *Polyblending.* Blends of semicompatible plastics often combine the best properties of the individual components [7]. Such polyblending has been particularly successful with commodity and engineering thermoplastics. It has not received much study on cellulosics. Very possibly it could broaden the range of properties and uses for these materials.

11. *Grafting.* There have been many studies on grafting onto the cellulosic backbone. Most of them were primarily theoretical in nature. With our modern grafting and polyblending technology, it is appropriate to reexamine this entire subject from the point of view of useful practical properties and applications.

12.   *Thermosetting Plastics.*   Commercial cellulosic plastics have been primarily thermoplastic.   With abundant hydroxyl (and acetal) functionality, it should be easy to synthesize a variety of thermosetting plastics with cellulosic backbones, and thus produce a wide range of increased heat and chemical resistance for new applications.

13.   *Stabilization of the Acetal Linkage.*   In aging degradation of cellulosic plastics, the acetal linkage is the weak point which leads to low molecular weight and loss of strength and chemical resistance.   The fundamental organic chemistry of acetals should be examined to see what it might suggest toward the stabilization of this linkage and thus toward improved age-resistance of cellulosic plastics.

14.   *Glass Transition Temperature.*   The moderate glass transition temperatures of the commerical cellulosic plastics (43–125°C) [8], mean that they are neither rigid at high temperature, nor flexible at room temperature or below.   Basic study of structure-T_g relationships in cellulosics should illustrate ways of controlling them over a wider range.   Optimally it would be desirable to be able to produce high glass transition temperatures for engineering thermoplastics and low ones for flexible products.

Such studies could go a long way toward hastening the day when we can base much or all of our plastics production on perpetually renewable resources from the forest products industry, and thus insure a long-term balance between our modern technological society and our growing desires for a wholesome ecological balance with our natural environment.

REFERENCES

[1]   *Modern Plastics, 52* (1), 46 (1975).

[2]   R. D. Deanin, *Amer. Chem. Soc., Div. Chem. Marketing Econ., Prepr.,* Philadelphia, 1975, p. 144.

[3]   R. L. Wakeman, *The Chemistry of Commercial Plastics,* Reinhold, New York, 1947, p. 295.

[4]   J. A. Brydson, *Plastics Materials,* Van Nostrand, New York, 1966, p. 560.

[5]   I. S. Goldstein, *Amer. Chem. Soc., Div. Chem. Marketing Econ., Prepr.,* Philadelphia, 1975, p. 25.

[6]   R. L. Wakeman, *The Chemistry of Commercial Plastics,* Reinhold, New York, 1947, p. 28.

[7]   R. D. Deanin, A. A. Deanin, and T. Sjoblom, in *Recent Advances in Polymer Blends, Grafts, and Blocks,* L. H. Sperling, Ed., Plenum, New York, 1974, p. 63.

[8]   L. E. Nielsen, *Mechanical Properties of Polymers,* Reinhold, New York, 1962, p. 20.

CHEMICALS FROM CELLULOSE*

W. M. HEARON, CHENG FAN LO, and JOHN F. WITTE

*Chemical Research Laboratory, Boise Cascade Corp.,
Portland, Oregon, 97201*

SYNOPSIS

While the oxidation of cellulose by sodium metaperiodate to dialdehyde cellulose has been known for many years, conditions were developed for carrying out this reaction in a relatively short time. Recovery of the iodine from the product was 99.9% and a chemical procedure was devised for its reoxidation to periodate. Further oxidation of dialdehyde cellulose with nitrogen tetroxide in either liquid or gas phase gave di- or tricarboxy cellulose. Hydrolysis of tricarboxy cellulose produced equimolecular quantities of meso-tartaric acid and glyoxylic acid. The latter on reductive ammination produced glycine. All reactions proceeded quantitatively, or nearly so. As a starting material, cotton linters, bleached pulp, or paper mill primary sludge (consisting of essentially bleached pulp and clay) could be used.

INTRODUCTION

Because of the availability of waste cellulose (particularly from paper mill primary sludge) in the pulp and paper industry, research was instigated in Boise Cascade's laboratories on the possible production of simple, nonpolymeric chemicals from cellulose.

A survey of the existing literature revealed a paper by Head [1], who reported the oxidation of cellulose in three steps to a polycarboxy cellulose followed by hydrolysis to yield meso-tartaric acid. The sequence of reactions is given in scheme I.

The initial oxidation with nitrogen tetroxide proceeded to only 0.78 carboxyl groups per glucose unit (g.u.), and assuming all these carboxyl groups were in the 6-position, the overall yield was 28% of theory for meso-tartaric acid isolated as the brucine hydrogen salt. Besides the low yields, Head's procedure suffered from other operational problems. The oxidation at carbon atom 6 was not complete. The polycarboxy cellulose on oxidation with periodate went into solution, making recovery of iodine difficult. Finally, the subsequent oxidation with chlorite and hydrolysis gave a mixture from which it was difficult to isolate pure meso-tartaric acid, and no attempt was even made to recover the glyoxylic acid.

* Dedicated to Professor Dr. Karl Kratzl, University of Vienna.
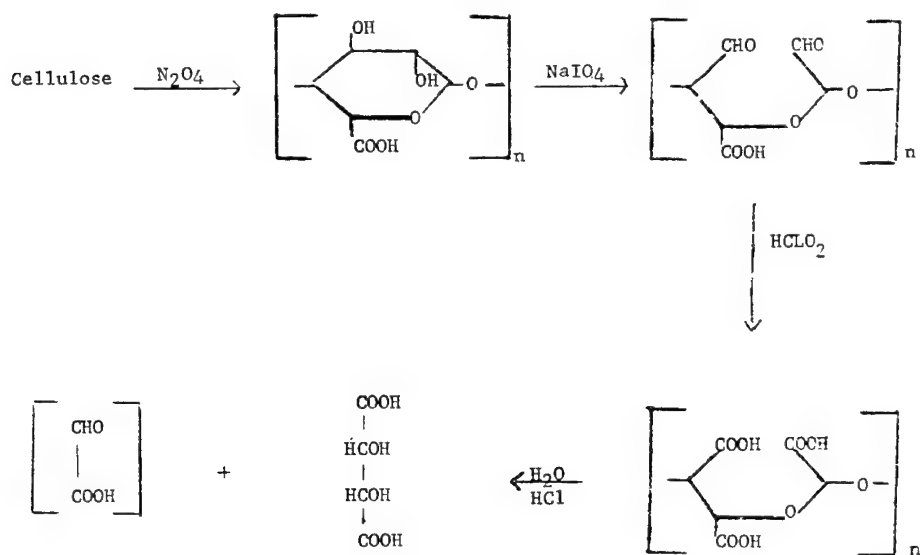
Scheme I

Our objective was to overcome these difficulties and devise a procedure which could have possibilities for commercial exploitation.

RESULTS

A first approach was to use nitrogen tetroxide under conditions drastic enough to produce carboxyl groups not only at carbon atom 6 but also at 2 and 3. However, when conditions were intensified—excess reagent, higher temperature, longer time, catalysts—oxalic acid was formed and no meso-tartaric acid could be detected. Other common oxidants gave the same result.

It was then decided to reverse the order of oxidation by starting with dialdehyde cellulose, and this change gave very satisfactory results. The sequence of reactions is shown in scheme II.
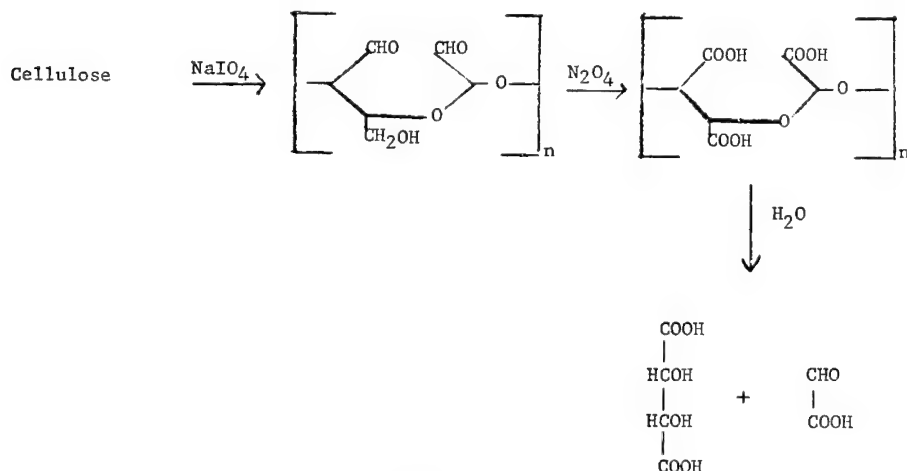
Scheme II

DISCUSSION

The oxidation of cellulose by periodate was first studied by Hudson et al. [2], and additional investigations were carried out subsequently by several other workers [3–6]. All procedures, however, required extended times and gave products of varying carbonyl content. Jackson and Hudson [7] proved that some, if not all, of the carbonyl groups were in the 2- and 3-positions.

We have found that the oxidation using 1.25 moles of periodate at about 50°C with bleached pulp at 8% consistancy in 5 hr yielded a product in 98% of theory containing essentially two and only two carbonyl groups per glucose unit. The product was insoluble in the reaction medium and could be readily recovered by filtration.

The commercial success of producing dialdehyde cellulose resides in part on the recovery and reuse of the iodine. It was found that under the conditions used, all the iodine existed as either unconsumed periodate or its reduction product, iodate. These chemicals could be recovered in the filtrate and washings of the dialdehyde cellulose in 99.9% molar yield.

The reoxidation of the iodate to periodate can be carried out electrolytically; this procedure is used in a commercial plant for producing dialdehyde starch. However, it is also possible to perform the oxidation with sodium hypochlorite. Since this reagent is made from components produced by the electrolysis of sodium chloride, and most of the salt formed when the hypochlorite is reduced can be recycled, this procedure is in essence an electrolytic reoxidation using salt as a carrier. The proposed iodate reoxidation process requires the precipitation of the iodate as the relatively insoluble paraperiodate to remove impurities. Scheme III is a graphic representation.

The oxidation of the dialdehyde cellulose was carried out using nitrogen tetroxide in either liquid or gas phase. For laboratory preparations the former is more convenient, but for commercial production the latter would be preferable. The oxidation proceeds stepwise with the more reactive aldehyde groups being oxidized first, and it is possible to isolate in good yields the dicarboxyl cellulose. Further oxidation gave products containing between two and three carboxyl groups per glucose unit. To arrive at a product containing essentially three carboxyls per glucose unit required careful control of conditions. If the temperature was allowed to rise much above 30°C in the initial oxidation, the theoretical carboxyl content for complete oxidation could not be reached because, we believe, of lactone formation between the 6-hydroxyl and a carboxyl group. If the oxidation was too vigorous, some oxalic acid was also formed which could be removed, however, by solvent extraction from the tricarboxy cellulose.

During the oxidation, the nitrogen tetroxide is reduced to nitric oxide which can be recovered, oxidized back to nitrogen tetroxide and reused. For the preparation of dicarboxy cellulose essentially no N_2O_4 need be lost, so the oxidation is performed by air. In the case of tricarboxy cellulose, oxidation of the primary hydroxyl group produces a mole of water which reacts with nitrogen tetroxide, so complete recovery of the oxidant is not possible.

The hydrolysis of the tricarboxy cellulose in water without a catalyst was incomplete at 100°C and above that temperature, the mixture darkened badly. Use of either sulfuric or hydrochloric acid accelerated the hydrolysis but also produced dark mixtures. Sulfurous acid, however, gave complete hydrolysis and a light-col-

IODINE RECOVERY
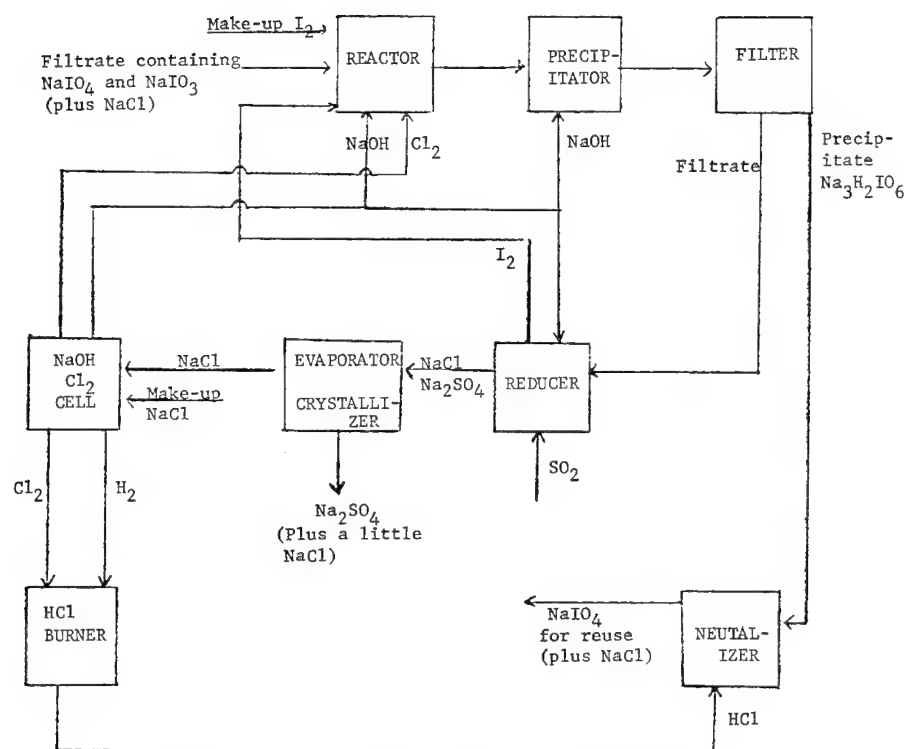
Scheme III

ored solution from which meso-tartaric acid and glyoxylic acid could be isolated.

The meso-tartaric acid was removed from the hydrolyzate with calcium ions. The free acid was easily recovered by removal of the calcium using sulfuric acid, oxalic acid, or cation exchange resins. On evaporation of the aqueous solution, meso-tartaric acid readily crystallized as the monohydrate. Based on the carboxyl content of the tricarboxy cellulose, essentially quantitative yields of meso-tartaric acid were obtained.

The quantity of glyoxylic acid in the filtrate after removal of the calcium tartrate was determined by the Cannizzaro reaction and confirmed by its oxidation to oxalic acid. Yields again approached the quantitative. Since glyoxylic acid has a very limited market, we explored the possibilities of converting it to valuable chemicals with established industrial uses. Glycine appeared to qualify. To our surprise, only one literature reference [8] was found for the reductive amination of glyoxylic acid to glycine. The yields were reported to be 8% and the glycine was isolated as the β-naphthylsulfonate. We found, however, that glyoxylic acid in 60% methanol with excess ammonia, hydrogenated at room temperature and moderate pressure and, using rhodium as a catalyst, gave pure white crystals of glycine in quantitative yields.

The precipitate was suspended in water (500 ml); calcium carbonate was added (3.0 g) and the pH adjusted to 1.8 with hydrochloric acid. Most of the suspended solid dissolved and the insoluble calcium oxalate (0.3 g) was filtered off. The filtrate was adjusted to pH 3.5 with 50% caustic. Ater 24 hr, the white precipitate was filtered off and thoroughly washed. After drying to constant weight at 100–105°C, the calcium meso-tartrate monohydrate weighed 7.519 g (94.0% of theory based on 0.7884 carboxyl groups in the 6-position).

The dry precipitate was suspended in water (200 ml) and a strong cation exchange resin added (30 ml). The precipitate quickly dissolved and the mixture was put in a column containing more of the same cation exchange resin. The eluate was collected until it was neutral, evaporated to a thin syrup and when scratched immediately crystallized. The white crystals were allowed to dry to constant weight at room temperature, giving 6.07 g of meso-tartaric acid monohydrate. (93.0% of theory based on 0.7884 carboyl groups in the 6-position.) The product had a neutralization equivalent of 84.5 (theory 84) and had a mp of 159°C which was not depressed by admixture with authentic meso-tartaric acid monohydrate.

The filtrate A was divided into two equal portions. One portion was taken to pH 12 with solid caustic, heated to 85°C for 3.5 hr and allowed to stand overnight at room temperature (24–25°C). The pH was taken to 1.0 with concentrated hydrochloric acid, treated with calcium carbonate (3.0 g), the pH adjusted to 1.8 with concentrated hydrochloric acid and allowed to stand for 24 hr. The precipitate of calcium oxalate was filtered off, dried at 100–105°C to a constant weight of 1.69 g (94.0% of theory).

The second portion of filtrate A was decationized, evaporated to 200 ml, the pH adjusted to 5.5 with sodium bicarbonate (2.8 g), and decolorized with activated carbon. The filtrate was treated with pure oxygen under vigorous stirring in the presence of 10% Pt on carbon (2.0 g). The pH dropped to 5.2 and was maintained between 5.2 and 6.5 by incremental additions of sodium bicarbonate. After a total of 3.75 g of bicarbonate had been added the pH rose to 8.2. The reaction was stopped, the catalyst removed and the oxalic acid precipitated by calcium at a pH of 1.0. The weight of calcium oxalate monohydrate was 2.55 g (70.9% of theory).

Oxidation of authentic glyoxylic acid using the identical procedure gave 77% of theory. Using this conversion factor, the yield of glyoxylic acid in the filtrate would be 92%.

Recovery of Meso-Tartaric Acid from its Calcium Salt

Besides the use of action exchange resins mentioned above, the calcium meso tartrate could be converted to meso-tartaric acid by metathesis with sulfuric or oxalic acid. The procedure was essentially the same. The calcium salt was mixed with an aqueous solution of the acid in slight excess to aid solution; the excess neutralized with lime and the precipitate filtered off. The filtrate was evaporated to a syrup and seeded. In the case of sulfuric acid, the syrup can be taken up in a little water and the small amount of calcium sulfate removed by filtration. Recoveries of meso-tartaric acid by these methods were in excess of 99% based on the calcium tartrate.

As a raw material for these syntheses, we used cotton, bleached pulp, and sludge from a paper mill primary clarifier. The last consisted of bleached pulp and fillers, mostly clay. This sludge varied in color from gray to yellow; however, the color was entirely removed during the oxidation with nitrogen tetroxide and the products were correspondingly colorless. The clay was removed by filtration when the tricarboxy cellulose was dissolved in water prior to its hydrolysis.

EXPERIMENTAL

Dialdehyde Cellulose

Preparation. To flash-dried bleached kraft pulp (6.4% water content) (69.2 g, 0.4 mole) in water (1000 ml) at 50°C was added sodium metaperiodate (107.0 g, 0.5 mole). The mixture was stirred briskly until the cellulose was well dispersed and gently thereafter while maintaining the temperature at 50°C. The pH was 4.6. After five hr, the dialdehyde cellulose was filtered off and washed with one 500-ml portion of water, two 200-ml portions of water, and two 200-ml portions of methanol. After air-drying, the product weighed 62.5 g or 97.7% of theory.

By consumption of periodate, the aldehyde content should have been 2.04 per glucose unit; by performing a Cannizarro's reaction using sodium hydroxide and back titrating the excess caustic, a value of 1.99 aldehyde groups per glucose unit was found.

Recovery of Iodine. The filtrate and aqueous washes from above were combined and analyzed for iodate and periodate. The iodate found was 0.4069 mole and periodate was 0.0917 mole, giving a recovery of 99.7%.

Reoxidation of Iodate. The filtrate and aqueous washes were evaporated to 500 ml volume, cooled and treated with sodium hydroxide (80 g, 2 mole). The solution was maintained at 95–100°C while chlorine was rapidly introduced until a slight excess was present.

The mixture was taken to pH 9.5 with 20% caustic and cooled at 10°C overnight. The precipitated sodium paraperiodate was filtered off and washed with four, 150-ml portions of 5°C water and dried at 110°C for 24 hr. The yield was 288.1 g or 98.0% of theory. The product had greater than 99.5% purity based on iodometric analysis.

The filtrate and wash waters were combined and the pH brought to 3 with concentrated sulfuric acid. Standardized sulfurous acid was then added until 0.035 mole was present. The iodine liberated was then distilled into 1N caustic and analyzed for iodine. Found was 0.009875 mole or 99.0% of theory. This iodine solution (together with any make-up iodine) could be reoxidized to periodate as given above for the reoxidation of iodate.

Dialdehyde Cellulose to Dicarboxy Cellulose

In a 1.5 in. I.D. 316 stainless steel pipe (6 in. long) was placed oven-dried dialdehyde cellulose (5.0000 g, 0.03125 mole, 2.1 aldehyde groups per glucose unit by periodate consumption), and the ends of the pipe were closed with caps provided with outlets. The pipe was flushed with oxygen and nitrogen tetroxide (1.15 g,

0.0125 mole) was introduced. The pipe inlet and outlet were connected to a circulating pump and oxygen was allowed to enter the system from a gas burette at essentially atmospheric pressure. The gases were circulated at the rate of 2–5 changes per minute and the temperature was maintained at 26–28°C. After 10 hr, 750 ml of oxygen had been absorbed (theory, 761 ml) and a longer time produced no additional oxygen take-up. The white dicarboxyl cellulose was removed from the pipe, washed twice with ether and dried at 100°C to a constant weight of 6.01 g (theory, 5.99 g). The carboxyl content determined by reaction with excess standard caustic and back-titration was 47.00% (theory, 46.88%).

Dialdehyde Cellulose to Tricarboxy Cellulose

Vapor Phase. In a two-necked 500-ml flask was placed fluffed dialdehyde cellulose (10.00 g, 0.0625 mole) (2.00 aldehyde groups by periodate consumption). One neck was left open as a vent and the other was connected to a small flask containing nitrogen tetroxide (30 ml, 43.5 g, 0.4728 mole). The mixture was allowed to stand at room temperature (20–24°C) for 48 hr. The tricarboxy cellulose was removed, air-dried and extracted with ether in a Soxhlet for 30 min to remove any residual inorganic acids and oxalic acid. The extracted white product was dried at 90°C for 1 hr. The weight of the product was 12.8745 g (theory, 12.8231 g). The carboxyl content determined by the calcium acetate method was 64.50% (theory for three carboxyl groups, 65.53%).

Liquid Phase. In a one-liter three-necked flask equipped with a stirrer and dropping funnel were placed carbon tetrachloride (500 ml) and dialdehyde cellulose (16.00 g, 1 mole) (2.00 aldehyde groups by periodate consumption). The mixture was agitated and through the dropping funnel was added nitrogen tetroxide (15 ml, 21.72 g) (0.2364 moles) over a period of 30 min. Stirring was continued at room temperature (23–25°C) for 48 hr. The tricarboxyl cellulose was then filtered off, washed with carbon tetrachloride and dried for 2 hr at 105°C. The white product weighed 19.79 g, 97.7% of theory (20.26 g). The carboxyl content by excess standard caustic and back-titration was 63.73% (theory for three carboxyl groups, 65.53%).

Hydrolysis of Tricarboxy Cellulose

Tricarboxy cellulose (10.00 g, 0.04925 mole, 61.8% carboxyl, $\bar{M}_w$ 203) and 5.5% freshly prepared sulfurous acid (100 ml) were sealed in a glass tube and heated at 125–30°C for 3.5 hr. After cooling, the pale yellow solution was removed from the tube, diluted with 100 ml water and boiled until the vapors were neutral to litmus paper. The solution was treated with a small amount of activated carbon, filtered, and diluted to 700 ml with distilled water. The pH was 1.9. Calcium carbonate was added to a pH of 2.5. Upon seeding with calcium oxalate a small precipitate formed. The mixture was then taken to pH 4.2 with calcium carbonate and a heavy white precipitate formed. After leaving the mixture for 16 hr, it was filtered and the precipitate washed with distilled water. The filtrate and washings (A) were saved.

Glyoxylic Acid to Glycine

In a hydrogenation bottle were placed methanol (20 ml) and 5% rhodium on carbon catalyst (0.20 g). The bottle was shaken with hydrogen at 30 psig for 20 min. In a 100-ml graduated cylinder in an ice bath were placed methanol (30 ml) and liquid ammonia (10 ml, 8.17 g, 0.48 mole), followed by dropwise addition during 10 min of 38.8% glyoxylic acid solution (5 ml) diluted to 25 ml with water (2.4817 g of 100% glyoxylic acid, 0.03354 mole). The mixture was added to the hydrogenation bottle and pressured to 45 psig with hydrogen. The hydrogenation was carried out at 20–25°C for 7.5 hr at which time no more hydrogen was absorbed. The catalyst was removed by filtration, the filtrate evaporated to 10 ml under reduced pressure at 50°C and the product precipitated by addition of methanol (90 ml). After 6 hr, the mixture was filtered and the white crystals were washed with methanol and dried at 100°C for 1 hr. The product's weight was 2.4567 g (97.7% of theory). The mp was 232–233°C and was not depressed by admixture with authentic glycine.

REFERENCES

[1] F. S. H. Head, *J. Chem. Soc.*, 1135 (1948).
[2] E. L. Jackson and C. S. Hudson, *J. Amer. Chem. Soc., 59*, 2049 (1937).
[3] G. Jayme, M. Satre, and S. Maris, *Naturwissenschaften, 29*, 768 (1941).
[4] G. F. Davidson, *J. Textile Inst., 31*, T81 (1940).
[5] I. J. Goldstein, J. K. Hamilton, R. Montgomery, and F. Smith, *J. Amer. Chem. Soc., 79*, 6469 (1957).
[6] J. E. Slager, U. S. 3,086,969 (to Miles Laboratories, Inc.) April 23, 1963. *C.A. 59*, 11644 (1963).
[7] E. W. Jackson and C. S. Hudson, *J. Amer. Chem. Soc., 69*, 989 (1938).
[8] P. Desnualle and C. Fromagest, *Bull. Soc. Chem., 5*, 1.700 (1934).

TRENDS OF UTILIZATION OF PULPING SPENT LIQUOR IN JAPAN

JUNZO NAKANO

Department of Forest Products
University of Tokyo, 113, Bunkyo-ku,
Tokyo, Japan

SYNOPSIS

At present four sulfite mills are utilizing the sugars in pulping spent liquor, and seven sulfite mills and one sulfate mill are producing commercial lignins in Japan. Yeast-producing companies are now very active in utilizing the valuable chemical derivatives in yeast extractives, because yeast itself is far from economical production. This promising type of research is now proceeding rapidly and actively. Lignin from spent liquor has generally been used within a wide range of low-cost applications. It is true that a considerable amount of time and effort must be spent to overcome various problems in the utilization of lignin. Two examples are given to explain why the utilization of lignin is difficult. Moreover, the research trends of lignin utilization are discussed.

INTRODUCTION

The purpose of this paper is to introduce the present status of the utilization of pulping spent liquor in Japan. Figure 1 shows the four major islands comprising Japan. The total area of the four islands is about 372,000 km^2, a little larger than Norway or Finland. At present, there are four yeast plants in the dissolving sulfite mills. There are seven sulfite mills and one sulfate mill producing lignin.

UTILIZATION OF SUGARS

Table I shows the production of pulp yeast and related products in 1974. Each mill uses different wood species as pulp wood. Kojin Comp. has been using mangrove from tropical areas and solved the yeast color problem caused by the dark color of this wood. The annual production of dry yeast is about 26,000 tons, and one company now intends to increase the amount of production. The companies shown in Table I are eager to find valuable pharmaceuticals and biochemicals from yeast extractives, because yeast itself is not economical to produce at present. This promising type of research has just begun and is now proceeding very rapidly.

Ribonucleic acid (RNA) is extracted from pulp yeast in about 10% yield. As
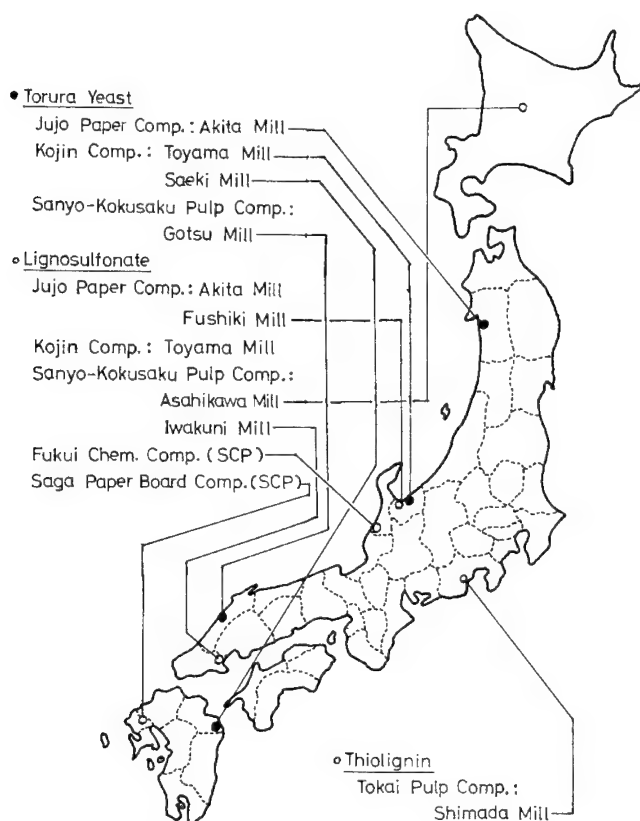
85

FIG. 1. Location of torula yeast and commercial lignin plants in Japan.

shown in Table II, the derived products from RNA are classified into four items. Among them, inosine monophosphate (IMP) and guanosine monophosphate (GMP) are well-known as chemical seasonings.   Yeast-producing companies are now very active in developing derived products of RNA; namely, anticancer or antivirus agents, etc.

UTILIZATION OF LIGNIN

There is a basic concept for developing utilization of lignin in that lignosulfonate has been used as a dispersant because of its sulfonic acid group, and thiolignin has been used as a resin ingredient because of its phenolic hydroxyl groups. However, the chemical field in which lignin can be utilized with benefit and success, has not been realized except for vanillin production from lignosulfonate. Lignin from spent liquor has been utilized in the wide range of low-cost applications.

Commercial Lignosulfonate

Calcium-base sulfite mills have been the major suppliers of lignin products. Figure 2 shows the production of sulfite spent liquor at 50% solids and of lignosul-

TABLE I
Production of Pulp Yeast and Related Products in Japan, 1974

Company	Pulp wood	Products t/M			
		Dry yeast	Yeast,50%	RNA	Purified RNA
Kojin	Mangrove	1,000		80	0.2
Jujo	Beech	750	60	15	?
Sanyo-Kokusaku	Mixed hardwood	400		30	?

Dry yeast: for animal feeds and fermentation
Yeast,50 % solids: for fermentation
RNA: for food additives and fermentation
Purified RNA: for pharmaceuticals and biochemicals

TABLE II
Derived Products from RNA

(1) Seasonings : IMP, GMP
(2) Drugs : Anti-leukemia, Anti-cancer,
            Anti-virus, Immuno suppressor,
            Cardiovascular
(3) Plant hormons
(4) Others: Hormon mediator, Vit. B_{12}-Coenz.,
            Psycostimulant

Pulp yeast ┬─ Denucleated yeast
           ├─ RNA(ca10% yeast basis)
           └─ Minor components: GSH, CoA,
              NAD, CoQ, CytC, Uricase

fonate in Japan over the period 1966–1973. The latest data in 1973 show that the production of spent liquor at 50% solids is about 140,000 tons, and the production of lignosulfonate is 18,000 tons.

There are many markets for lignin products. More than fifty commercial lignins are produced to meet the market needs in Japan. In general, lignosulfonate has the capacity to act as either a dispersant or a binder, and desugared sulfite liquor is the best dispersant. As shown in Table III, lignosulfonate has been mainly used to reduce the power requirements in the wet cement process, to improve the workability and the strength of concrete, and as a binder for fine ores, ceramics,
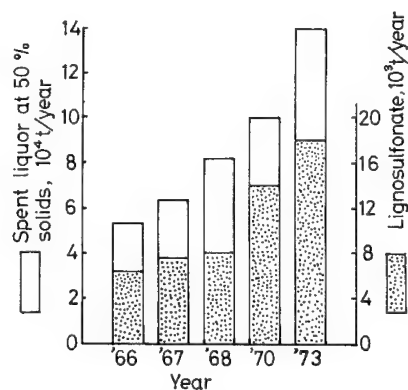

FIG. 2. Production of spent liquor at 50% solids and lignosulfonate in Japan, 1966–1973.

TABLE III

Use of Lignosulfonate in Japan, 1973

Uses of LSA	Sales of LSA solids, 1000t/year	%
Concrete additives	34	33
Binder for fine ores	31	30
Cement additives	11	11
Binder and dispersant for ceramics	6	6
Binder for fertilizer, Soil conditioners	5	5
Dispersant for dyestuffs	3	3
Binder and dispersant for insecticides	2	2
Dispersant for oil well drilling muds	2	2
Plasterboards additives	1	1
Resin ingredients	1	1
Binder for foundry molds	1	1
Others	5	5
Total	105[a]	100

[a] Including imported commercial lignin.

insecticides, foundry molds, and so on. Total sales of lignosulfonate in 1973 was 105,000 tons/yr including imported commercial lignin. Table IV shows the amount of imported and exported commercial lignins. A large portion of these lignins is lignosulfonate and is used mainly as concrete additives.

Commercial Thiolignin

The production of thiolignin is only 100 tons/month at present, although about 300 tons/month of thiolignin were produced several years ago. At that time, thiolignin was manufactured by three companies. As shown in Table V, thiolignin is used mainly as a phenol resin ingredient and a dispersant. The latter is used after sulfomethylation with sodium sulfite and formaldehyde.

RESEARCH TRENDS IN UTILIZATION OF LIGNIN

Figure 3 shows the papers and patents in the field of lignin utilization. These were published from 1950 to 1962 and from 1970 to 1972, and collected from Chemical Abstracts. Some information about the research trends of lignin utilization is obtained from this figure.

TABLE IV

Imported and Exported Commercial Lignins in Japan (ton)

Commercial lignin	1971	1972	1973	1974[c]
Imported[a]	6,513	9,081	15,095	14,588
Exported[b]	1,286	1,224	1,170	1,042

[a] Concrete additives.

[b] Concrete additives, dispersant for oil-well-drilling muds, etc.

[c] January–September.

TABLE V
Production of Thiolignin in Japan, 1973

Tokai Lignin (Trade name)	Production t/M	Uses
F	45	Phenol resin[a]
B	45	Dispersants[b]
S,F,B	10	Others[c]

[a] Plywood, shell mold, etc.

[b] Disperse dye, pigments and insecticides.

[c] Binder, storage battery plates, protein precipitants, etc.

There are about 600 papers and patents in the period 1950–1962, and 190 papers and patents in the period 1970–1972. In these papers and patents, the utilization of hydrolysis lignin is not included. For convenience, the field of utilization was classified into nine sections as follows: isolation, dispersants, agricultural use, ion exchanger, tanning agents, and so on. It is very interesting to compare how the research trends changed during these two periods.

Comparing the research tendency of both periods, it is worth noting that the Soviet Union is very active in lignin utilization. Among 190 papers and patents appearing in the period 1970–1972, about 60 are from the Soviet Union. Moreover, about 40 papers in the utilization of hydrolysis lignin were also from the Soviet Union in 1970–1972. As a whole in 1950–1962, the research was aimed at developing the lignin utilization in the field of resin and adhesives, and as to the degradation products, vanillin production was mainly studied.

Other fields increased very much in importance in 1970–1972. This means that researchers have been active in developing other means of utilizing lignin. This includes studies on carbon fiber, slurry explosive, fire-extinguishing compounds, etc.

In counting the number of papers and patents from each country in 1970–1972, there are about 100 from the Soviet Union, 50 from the United States, 30 from Japan, 20 from West Germany, and 5 from Canada. It is worth noting that Sweden, a pioneering country in wood chemistry and pulp and paper technology did not contribute any paper or patent.
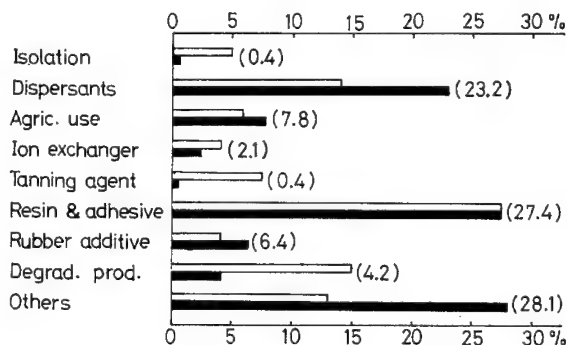

FIG. 3. Papers and patents in the field of lignin utilization collected from Chemical Abstracts: □ 1950–1962, ■ 1970–1972. Data in ( ): % in 1970–1972.

TABLE VI
Shearing Strength of Lignin Epoxide Cured with Phthalic Anhydride
(*J. Japan Wood Res. Soc., 13* (6), 1967)

Resin	Epoxy value eq./100g	Hardner %	Resin mg/cm²	Shearing strength,kg/cm² Min.	Max.	Av.	Failure[a] %
L[b]	0	10.0	5.5	14.8	21.9	17.3	0
LE[c]	0.10	11.8	6.7	38.9	51.3	45.6	0
	0.14	16.6	5.9	54.5	80.0	62.8	20
	0.16	19.2	7.4	65.9	80.0	74.5	60
	0.19	22.6	6.2	44.9	69.9	57.1	0
PLE[d]	0.28	33.3	4.9			80.0	100
ALE[e]	0.17	20.4	6.6	24.7	39.9	29.6	0
HLE[f]	0.16	19.2	7.0	26.2	40.3	35.1	0

[a] Alminium (90 × 25 mm) failure: 80 kg/cm²<

L: Thiolignin; LE: Lignin epoxide; PLE: Phenolated lignin epoxide; ALE: Epoxide of bisquaiacylated lignin with acetone; HLE: Epoxide of bisquaiacylated lignin with methyl hexyl ketone.

SOME LIGNIN PROPERTIES FROM THE VIEWPOINT OF UTILIZATION

The present methods of utilization of lignin do not easily meet new markets needs. On this matter, two examples will be given as an explanation.

The first concerns lignin as a resin ingredient. There are many proposals on this point. The use of lignin, however, is very much limited because of its high viscosity and dark color. The former lowers the production efficiency and the latter limits the field of usage. In addition to these facts, another problem is illustrated in Table VI [1]. This table shows the shearing strength of various types of lignin epoxides cured with phthalic anhydride. An aluminum test piece was used instead of wood, because lignin epoxide showed a very high shearing strength. However, a good, cheap solvent for this resin could not be found.

The second example concerns lignin as an industrial chemical. Vanillin production from lignosulfonate has been carried out since the late 1930s. Considering the present and future situation of vanillin as a raw material for pharmaceuticals, vanillin and related compounds are showing evidence of greater potential. The degradation research of lignin should be developed more actively; it is again attracting attention since the oil crisis. However, until now, as a result of research on lignin degradation reactions, a great many products have been obtained. This is why the field of lignin utilization has been difficult to develop.

TABLE VII
Phenols in Acidic Oil Produced by Hydrogenation of Lignosulfonate (Govern. Forestry Exp., 1966)

(1) Guaiacol (1.6~1.9)   (2) Phenol (4.1~6.3)
(3) o-Cresol (4.4~5.0)   (4) m-,p-Cresol (12.9~20.0)
(5) o-Ethyl phenol + 2,4-Xylenol (6.3~9.3)
(6) Propyl guaiacol (0.9~1.5)
(7) m-,p-Ethyl phenol (3.2~5.8) (8) 3,4-Xylenol (3.2~5.8)
(9) p-Propyl phenol (5.6~5.8) (10) Catechols (5.6~13.6)

Yield of acidic oil: 10~12%, lignin basis
Data in ( ): %, acidic oil basis
Catechols: Catechol, Methyl(Ethyl, Propyl) catechol

The results of research performed by Government Experiment Station, Japan in the 1960s, is summarized in Table VII [2]. This table shows the phenols in acidic oil produced by hyrrogenation of lignosulfonates. Hydrogenation was done as a continuous operation. The experimental conditions were as follows: temperature, 370°C; time, 120 min; pressure, 280 kg/cm^2; catalyst, iron carbonyl Fe(CO)$_5$. Continuous hydrogenation resulted in the identification of more than ten phenols, but these were not obtained in good yields. Moreover, an economical way to isolate these phenols could not be found. Evidently, a new process by which valuable degradation products can be produced in simple steps and in a large quantity with good yield, awaits to be developed.

REFERENCES

[1] S. Tay, J. Nakano, and N. Migita, *Mokuzaishi, 13,* 257 (1967).

[2] M. Miyazaki et al., *Bull. Gov. Forest Experiment Station, No. 195,* 57 (1966).

MANNOSE CHEMICALS

F. W. HERRICK, R. L. CASEBIER, J. K. HAMILTON, and
J. D. WILSON

Olympic Research Division,
ITT Rayonier Incorporated,
Shelton, Washington 98584

SYNOPSIS

The purpose of this study was to develop economic processes for recovering mannose or its derivatives from wood resources where it is a major component of mixtures containing other carbohydrates and lignin fragments. Five mannose chemicals were considered: D-mannose, the sodium bisulfite adduct of D-mannose, methyl α-D-mannopyranoside, sodium D-glycero-D-galacto-heptonate, and D-mannitol. The main achievement of this work was the development of processes for recovering sodium mannose bisulfite and methyl mannoside from several raw materials. Mannose was obtained by regeneration of sodium mannose bisulfite and converted to mannitol and sodium D-glycero-D-galactoheptonate using known procedures. Sodium mannose bisulfite was prepared in nearly quantitative yield from the mannose component of spent sulfite liquor or from mannose-containing polymers by sulfurous acid hydrolysis and subsequent treatment with sodium hydroxide. Production of methyl mannoside involved hydrolysis of mannose-containing polymers by methanolysis concurrent with glycosidation. The economics and markets for these and other mannose chemicals are discussed.

INTRODUCTION

D-mannose, either alone or in combination with other sugars, is a common constituent of polysaccharides from plants and microorganisms. Mannose occurs most frequently as a heteropolymer with glucose and/or galactose in glucomannans, galactoglucomannans, and galactomannans. It is also found as a homopolymer in the mannans derived from vegetable ivory nuts and certain seaweeds.

Five mannose chemicals are discussed in this paper: D-mannose, the sodium bisulfite adduct of D-mannose, methyl α-D-mannopyranoside (methyl mannoside), sodium D-glycero-D-galactoheptonate (sodium mannoheptonate), and D-mannitol. Only the last of these compounds is also found widely in nature, such as in tree and shrub exudates or saps (plane tree exudate: 80–90% mannitol), fruits, leaves, bulbs, fungi and algae. Collection and extraction of mannitol from these resources is not presently commercially competitive with other processes.

Spent liquors generated by conifer wood-pulping processes are rich in mannose.

93

TABLE I
Composition of Sodium-Base Spent Sulfite Liquor

Percent by weight, dry solids basis		
Sodium lignosulfonate		61.5
Carbohydrates:	Monomeric	Total
Galactose	3.1	3.8
Glucose	3.3	5.5
Mannose	12.1	14.2
Arabinose	1.5	1.5
Xylose	3.3	3.3
Total	23.3	28.3

TABLE II
Composition of Prehydrolysis Liquor from Southern Pine Wood

Percent by weight, dry solids basis		
Carbohydrates:	Monomeric	Total
Galactose	3.0	9.2
Glucose	1.6	12.0
Mannose	3.5	38.4
Arabinose	3.2	2.5
Xylose	5.6	9.8
Total Carbohydrates	16.9	71.9

RAW MATERIALS : WOOD SUGARS AND THEIR POLYMERS
PRESENT IN PULP MILL LIQUORS.
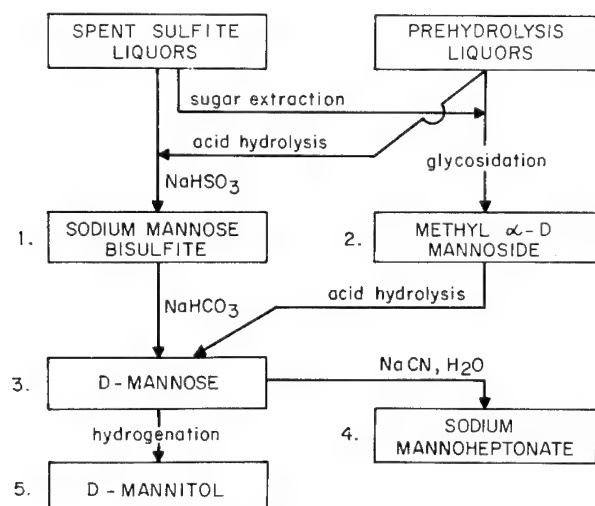
FIG. 1. Mannose chemicals.

Such carbohydrates, whether monomeric or polymeric, are derived from the "hemicellulose" portion of the wood [1]. In conifers, mannose is the predominant sugar unit in prehydrolysis extracts of wood [2,3] and in the carbohydrate fraction of spent sulfite liquor (Tables I, II), amounting to about 40% of total carbohydrates, based on hydrolysis to and analysis of monomeric sugars [4]. Current production of sulfite pulps in North America would indicate the availability of a mannose resource in spent sulfite liquor of 400,000 ton/yr.

The objective of the investigation described in this paper was to develop economic processes for recovering mannose or its derivatives in relatively pure form, given that the raw materials contain many component sugars, isomers, polymers and major lignin contaminants. This objective was achieved and practical, selective processes were devised for recovering mannose from crude mixtures via two routes: (1) formation of the sodium bisulfite adducts of monomeric wood sugar mixtures, crystallization and separation of sodium mannose bisulfite [5], and regeneration of mannose from this intermediate; and (2) anhydrous methanolysis concurrent with glycosidation of crude mixed-sugar polymers or monomers, crystallization and separation of methyl α-D mannoside [6,7] and regeneration of mannose from this intermediate. Figure 1 is a schematic illustration of the manner in which five mannose chemicals were obtained.

EXPERIMENTAL

Conversion of Wood Prehydrolyzate to a Monomeric Wood-Sugar Syrup

Mild H_2SO_4 Hydrolysis. A 38-liter volume of prehydrolyzate from southern pine wood chips, containing 5% solids and the composition given in Table II, was hydrolyzed with 0.5% H_2SO_4 w/v by stirring in a stainless steel pressure vessel at 110°C for 4 hr. Water-insoluble material was filtered off. The solution was then deionized by ion exchange and concentrated to a syrup having a pH of 2.6 and 79.5% total solids. The composition of this syrup is shown in Table III.

Sulfurous Acid Hydrolysis. Concentrated prehydrolyzate, 500 g, 51.9% solids, was diluted with 2 liters of water containing 60 g of SO_2. This mixture contained about 10% total carbohydrate solids, had a pH of 1.8, and was heated at 110°C for 4 hr. The resulting solution was neutralized with NaOH equivalent to the forma-

TABLE III

Composition of Wood Sugar Syrup Prepared from Prehydrolysis Liquor by Acid Hydrolysis

Percent by weight, dry solids basis	
Monomeric Sugars	
Galactose	15.9
Glucose	15.9
Mannose	40.3
Arabinose	8.0
Xylose	15.2
Total	95.3

HERRICK ET AL.

tion of sodium bisulfite. Analysis indicated that 72% of the total carbohydrate, as shown in Table II, was converted to monomeric sugars. Mannose content on a solids basis was 21.8%.

Crystallization of Sodium Mannose Bisulfite from Various Monomeric Wood-Sugar Mixtures

From Spent Sulfite Liquor. Sodium base liquor of the composition shown in Table I was concentrated to nominally 50% solids in a commercial evaporator. A charge of 36.36 kg of concentrate, containing 48.3% solids and 2.18 kg of mannose by analysis, was treated with 4.91 kg of sodium metabisulfite dissolved in 9.64 kg of water. This mixture was heated to 65°C, diluted with 28.4 kg of methanol and seeded with 50 g of crude powdered sodium mannose bisulfite. The mixture was stirred slowly and cooled at a rate of 12°C/hr over a 4-hr period, during which the mixture became viscous with massive fine crystallization of sodium mannose bisulfite (Fig. 2).
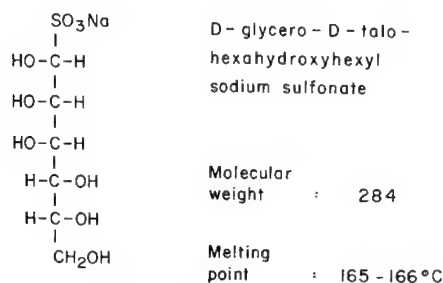
FIG. 2. Sodium mannose bisulfite.

The entire mixture was then drained into a fine cotton-cloth filter in a vacuum filtration apparatus. The recovered filter cake of crude product weighed 9.91 kg and contained 41% solids, equivalent to a dry yield of 4.06 kg. On a dry basis this crude product contained 11.5% sodium lignosulfonate and 50% mannose. Purity based on mannose content was 79% and recovered yield corresponded to 93% of

TABLE IV

Composition of Sodium Mannose Bisulfite Crystallized from Spent Sulfite Liquor

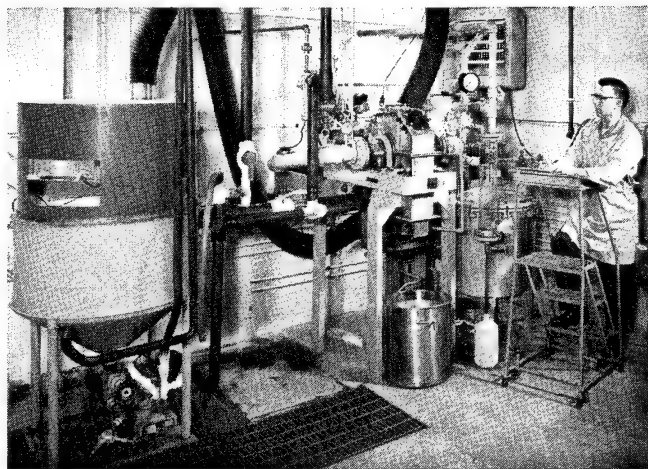| Percent by weight, dry solids basis		
	Crude	Purified
Na lignosulfonate	5.90	0.30
Galactose	0.22	–
Glucose	0.00	–
Mannose	54.50	58.80
Arabinose	0.06	–
Xylose	0.18	–

FIG. 3.

the mannose in the raw material. Other batches of crude product had the composition shown in Table IV. Reslurrying of the crude product in hot 1:1 w/w methanol-water yielded a white product containing only 3% sodium lignosulfonate.

Recrystallization of crude product, after filtration of solution through an adsorbent, resulted in a purified snow white crystalline sodium mannose bisulfite having the composition shown in Table IV. Mannose analysis of purified products seldom exceeded 59%, indicating some discrepancy between the calculated value of 63.38% mannose in a "theoretical" pure compound, as compared with laboratory samples. The melting points of purified products were identical to that of sodium mannose bisulfite prepared from pure mannose (165–166°C).

Sodium Mannose Bisulfite from Mixed Wood-Sugar Syrup Derived from Pine-Wood Prehydrolyzate by Mild H_2SO_4 Hydrolysis. A syrup of a type similar in composition to that shown in Table III, but without purification, was found to contain 28% mannose by analysis. A 2-liter volume of syrup containing 38.2% solids and having a specific gravity of 1.165 was stirred while 456 g of sodium metabisulfite was added. After standing overnight, the solution was filtered to recover off-white crystals of crude product. The wet cake was slurried in 1 liter of methanol and refiltered and washed with methanol. The final product (423 g) contained 45% mannose on a dry basis, representing 79% recovery of mannose. Other sugar bisulfite adducts, expressed as sugars, were present to the extent of 4% hexoses and 2.8% pentoses.

Sodium Mannose Bisulfite from Mixed Wood-Sugar Syrup Prepared by H_2SO_3 Hydrolysis of Pine Wood Prehydrolyzate. A wood-sugar syrup prepared by SO_2 hydrolysis is described above. An aliquot representing 0.9 of the volume yield (2142 ml) was concentrated to 500 ml by vacuum evaporation. Sodium metabisulfite was added to provide 45% by weight of $NaHSO_3$ based on the original prehydrolyzate solids. After cooling and overnight crystallization, crude sodium mannose bisulfite was recovered by filtration and washing with 1 liter of methanol. The dry product had a melting point of 160–163°C and weighed 168 g, corresponding to a recovered yield of 95% based on the mannose analysis of the original prehydrolyzate.

Crystallization of Methyl α-D-Mannopyranoside (Fig. 4) from Several Mannose Raw Materials

Direct Crystallization from Crude Glycosidation Mixtures. Prehydrolyzate from southern pine wood having the composition shown in Table II was obtained at 5% solids and was concentrated to about 40% solids by evaporation. This syrup was then spray-dried using an inlet hot-air temperature of 154–165°C, an outlet air temperature of 75–85°C, and a chamber temperature of 91–98°C. A 200-g quantity of spray-dried prehydrolyzate solids was refluxed (65°C) with 400 ml of anhydrous 3.0% methanolic HCl for 4.5 hr. The reaction mixture was filtered and the filtrate refrigerated at −15°C. Crystalline methyl mannoside formed gradually during a period of one week and 13.5 g of product was recovered by filtration, corresponding to 17.6% recovery of mannose based on that present in the raw material. Treatment with activated carbon and recrystallization from 4:1 v/v ethanol-water yielded a relatively pure product melting at 190–193°C as compared with 192–193°C for an authentic sample.

Rapid Methanolysis and Glycosidation of Wood Prehydrolyzate and Recovery of Crystalline Methyl Mannoside and a Syrup of Purified Mixed Wood-Sugar Methyl Glycosides. A 2.5-kg charge of the same spray-dried prehydrolyzate as used above was mixed with 5 liters of 6% methanolic HCl in a tantalum metal-lined, steam-heated tumbling autoclave, heated to 91°C and a pressure of 3.71 kg/cm^2 (53 psi) and held at this temperature for 15 min. In order to determine optimum reaction conditions, samples of 400 ml of reaction mixture were removed at several reaction times in the range of 15–240 min. Each sample was weighed, neutralized to pH 7 with 5N methanolic KOH and concentrated to a viscous syrup by vacuum evaporation at 50°C. This syrup was dispersed in 200 ml of warm water and a water-insoluble material was removed by filtration through No. 1 Whatman paper. Next, the water-soluble fraction was decolorized by boiling with activated carbon and filtered. At this stage the solution contained about 25% solids and was used both for analysis and crystallization to recover methyl mannoside. Analyses were carried out by converting the sugar glycosides to trimethyl silyl ethers which were determined by gas chromatography [8].

To recover crystalline methyl mannoside, the mixed-sugar glycoside solution was concentrated to 75% solids, refrigerated at 0°C for two days and filtered. Analysis of the solution withdrawn from the above 15-min autoclave reaction indicated a weight-yield value of 30.65% methyl mannoside in the product solution, corresponding to 74% conversion of the mannose raw material. The weight yield
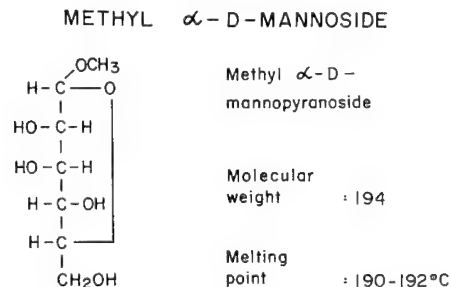
METHYL α – D – MANNOSIDE

FIG. 4. Methyl α-D-mannoside.

of crystalline product was 27.5% based on the weight of the original prehydroly-
zate solids, or 89.6% recovery of the methyl mannoside available in the reaction
mixture. The weight yield of mixed methyl glycoside remaining after the separa-
tion of methyl mannoside was 67.3% of the original raw material. A fairly broad
range of reaction conditions were shown to be useful on the basis of this type of ex-
perimentation [6].

Glycosidation of a Monomeric Wood-Sugar Mixture. A syrup prepared by
mild H_2SO_4 hydrolysis of pine-wood prehydrolyzate as described above, and hav-
ing the composition shown in Table III, was dehydrated by azeotropic distillation.
A 126-g sample of the syrup, representing 100 g of sugar solids was treated with
125 ml of toluene in a solvent recycle, water-trap apparatus. The toluene water
azeotrope, boiling at 84°C, was distilled until all water had been removed. After
cooling, the remaining free toluene was poured off, 200 ml of methanol was added
and the toluene-methanol azeotrope, boiling at 64°C, was distilled until the re-
maining toluene was removed. Enough concentrated methanolic HCl was then
added to provide at least 200 g of 3% methanolic HCl for glycosidation and the re-
action mixture was refluxed for 8 hr. Crystallization of methyl mannoside was
promoted by refrigeration. The weight yield of methyl mannoside was 20% based
on the starting material solids, representing 46% recovery based on mannose anal-
ysis.

Glycosidation of Wood Sugars in Spent Sulfite Liquor. A 1.08-kg quantity of
spray-dried sodium-base spent sulfite liquor, having a composition similar to that
shown in Table I and 5% moisture content, was heated with 2.38 kg of methanol
containing 0.25% HCl to boiling for 30 min with stirring. The liquid phase was
decanted through a filter and the residue was reextracted twice with 0.4 kg of the
same solvent and using the same conditions. The filtered methanol-HCl extract
was then processed to recover and recycle the major portion of the solvent, while
yielding 1.34 kg of extract concentrate syrup containing 57.4% solids, correspond-
ing to about 75% of the original dry raw-material weight and a high yield of mono-
meric wood sugars. The extract syrup contained 16.1% mannose and 31% total
sugars. The purpose of this extraction step was to remove methanol precipitable
lignosulfonate material prior to glycosidation.

A 174-g portion of the spent sulfite liquor extract syrup, containing 100 g of ex-
tract solids, was treated with 100 g of 6% methanolic HCl at reflux for 5 hr. The
cool reaction mixture was seeded with a trace of methyl mannoside and refrigerat-
ed for five days. Crude product (10.5 g) was recovered by filtration and washing
with cold methanol. Pure methyl α-D-mannopyranoside was obtained by recrys-
tallization in a yield corresponding to recovery of 50% of the mannose in the ex-
tract syrup.

Regeneration of Mannose from Sodium Mannose Bisulfite

Sodium Bicarbonate Reagent. A crude sodium mannose bisulfite, having a
composition similar to that shown in Table IV but containing only 3% sodium lig-
nosulfonate, was used as starting material. A dry equimolar blend containing
2272 g (8 mole) of sodium mannose bisulfite (calculated from analysis) and 672 g
of sodium bicarbonate was placed in a tall vessel equipped with a stirrer and a
steam-heating coil. A paste of the reagents was formed by adding 2 liters of hot

water, while stirring and heating the reaction mixture at 90°C for 16 min. Evolution of CO_2 was nearly complete during this step. The frothy mixture was then stirred and extracted with 16 liters of hot ethanol at 70°C for 10 min. The hot alcohol solution of crude mannose was filtered at once to remove 934 g of sodium sulfite by-product and insoluble impurities. The hot, slightly alkaline filtrate was then neutralized with 40 g $CaCl_2$ dissolved in aqueous ethanol, and precipitated material was filtered off. Rapid workup of the above reaction mixture was necessary in all steps prior to neutralization to minimize alkaline epimerization of mannose.

The relatively pure mannose solution was heated (stripped) to recover ethanol and concentrated to a volume of 1.2 liters. The product solution was clear and colorless and had a pH of 6.8, 73.5% solids and a specific gravity of 1.387. This syrup had a solution concentration of 73% mannose at a purity of 99+%, corresponding to 85% recovery of mannose from the sodium mannose bisulfite present in the starting material (Fig. 5).

Sodium Hydroxide Reagent. A solution of 80 g of sodium hydroxide in 500 ml of water was added rapidly with stirring to dry crude material, as used in the above procedure and containing 568 g of sodium mannose bisulfite, at a reaction temperature of 75–80°C for 10 min. This mixture was extracted with 4 liters of hot ethanol, while stirring at 75°C for 10 min, and filtered immediately. The amber-colored filtrate (pH 9.6) was treated with 10 g of $CaCl_2$ dissolved in 67 ml of 3:1 v/v ethanol-water and precipitated material was filtered off. Ethanol was recovered by distillation while yielding 421 g of orange-colored syrup containing 64.3% solids or 75.2% recovery based on the mannose content of the starting material. This product was relatively pure with respect to mannose but contained small amounts of glucose and fructose.

Preparation of Sodium Mannoheptonate and Mannitol from Mannose

Sodium D-glycero-D-galactoheptonate. A wood-sugar syrup prepared by sulfuric acid hydrolysis of pine-wood prehydrolyzate, as described previously, was found to contain 82% solids. On a solids basis, monomeric sugar composition was: 11.6% galactose, 10.8% glucose, 22.5% mannose, 12.8% arabinose and 16.6% xylose. A 244-g sample of this syrup was treated with 49.4 g NaCN dissolved in 175 ml H_2O. The mixture was stirred at 24°C for 16 hr after which NaOH was added to pH 12 and the solution was heated to boiling. This solution was refrigerated at 5°C for crystallization. Crude sodium mannoheptonate was recovered by filtration and washing with 4:1 v/v methanol-water and finally with cold methanol. Product yield was 34 g or 55%, based on the mannose content of the original syrup. The purity of the product was 98% based on aldonic acid analysis by a hydroxamic acid-ferric chloride method [9] using authentic sodium D-glycero-D-galacto-heptonate (Fig. 6) for calibration purposes.

D-Mannitol (Fig. 7). A solution of mannose was prepared by treating sodium mannose bisulfite (28.4 g) with calcium chloride (5.16 g) and 200 ml of water. After refluxing for 7 hr with evolution of SO_2, the solution was filtered to remove a white precipitate of calcium sulfite and other insoluble products (6.1 g). One-half of the mannose containing filtrate was diluted to 125 ml and pH was adjusted

D- mannopyranose

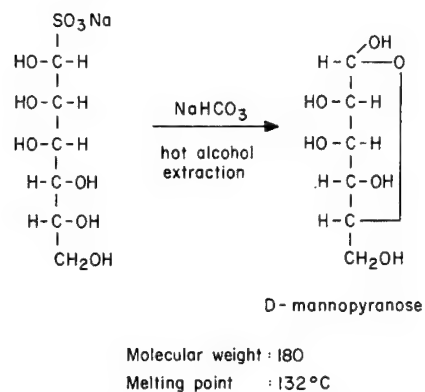Molecular weight : 180
Melting point : 132 °C

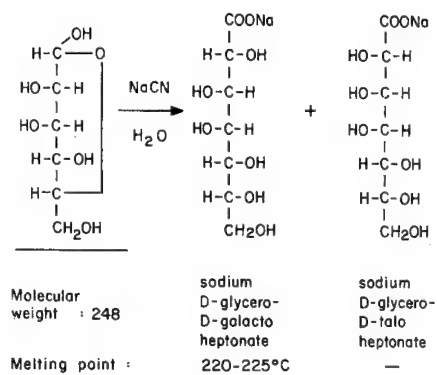FIG. 5. D-mannose from sodium mannose bisulfite.

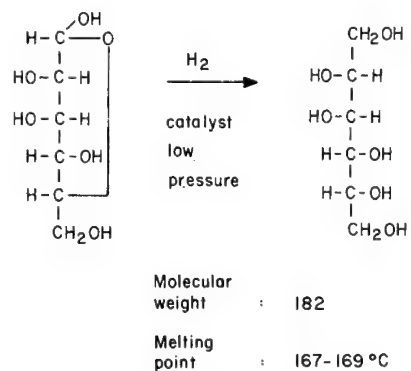FIG. 6. Sodium mannoheptonate via Kiliani synthesis.

FIG. 7. D-mannitol via hydrogenation of D-mannose.

to 8.0. After addition of 10 g of Raney nickel catalyst, the solution was hydrogenated at room temperature and a pressure of 3.43 kg/cm^2 (49 psi) for 8 hr. The resulting solution was filtered to recover catalyst and evaporated to dryness. The white crystalline solid was recrystallized from methanol-water to recover 3.9 g of mannitol or 43% yield based on the mannose content of pure sodium mannose bisulfite.

RESULTS AND DISCUSSION

The name "mannose" is derived from the biblical "manna" by way of the more familiar mannitol, which is the main component of manna and many similar plant exudates [10]. From ancient times, such plant gums have been used as sweetening agents. Mannitol was probably observed in crystalline form prior to the development of sucrose as an article of commerce [11]. This sugar polyol, because of easy crystallization and lower water solubility, was the first to be "discovered" as early as 1806 [12]. Present commercial production of mannitol is based on the mild alkaline hydrogenation of invert sugar or glucose, where mannitol is recovered by crystallization from a mixture of sorbitol and mannitol [13,14], the latter being formed by the hydrogenation of fructose, or alternately, from mannose produced by alkaline epimerization of glucose [15]. Most recently, mannitol was crystallized from a hydrogenation product derived from mixed wood sugars extracted from spent sulfite liquor with methanol solvent [16].

The known separation of mannitol from sorbitol was the precedent for the investigation reported in this paper. The question was: could other mannose derivatives be used as a means for separating mannose from the crude wood sugars present in wood extracts such as spent sulfite liquor? The first approach taken was that involving glycosidation to form the methyl glycosides of all the sugar components; one advantage being that glycosidation conditions are also useful for hydrolysis of polysaccharides, such that mannose-containing polymers would also be converted to monomeric glycosides. This study was well along before a more straightforward procedure was devised for the desired separation via the wood-sugar-bisulfite adduct route. By either route, it was certainly not anticipated that the complex mixture represented by either spent sulfite liquor or wood prehydrolyzates could be made to yield a relatively pure mannose derivative. As a general rule, the fractional crystallization of monomeric sugar mixtures is discouraging and not practical because of mutual solubility properties and extremely low crystallization rate. There was no evidence in the literature that a practical means for separating mannose from four other wood-sugar components (Tables I–III) was either suggested or demonstrated.

Sodium Mannose Bisulfite

The structure of the bisulfite adducts of common sugars is illustrated in Figure 2. The assignment of a sulfur-carbon bond between the sugar and the "bisulfite" moiety is based on the work of Ingles [17]. It is now clear that the bisulfite derivative route provides a simple and practical means for separating the mannose derivative from spent sulfite liquors, or more generally from any mannose-containing monomeric sugar mixture.

In the case of spent sulfite liquor, which is predominantly a lignin derivative and contains variable amounts of sugars depending on the pulping process used, it is possible to isolate a crude sodium mannose bisulfite product having a purity above 80% and more usually above 90%, while recovery of mannose based on the analysis of the raw material is nearly quantitative. If a small compromise is made with regard to yield, crystallization times as short as 2 hr appear practical. This investigation was also carried through a pilot plant stage and study of a continuous crystallization process, wherein incremental process time was reduced considerably below 2 hr, without any sacrifice in yield, since continuous crystallization can be performed in stages. Figure 3 is a photograph of the pilot plant equipment, which includes a continuous crystallizer, a continuous vacuum-precoat filter and apparatus to recover and recycle methanol.

Separation of sodium mannose bisulfite from monomeric sugar bisulfite adduct mixtures was found to be rapid and less complicated than when dealing with spent sulfite liquor raw materials. Thus, wood-sugar mixtures derived from wood prehydrolyzates, ultrafiltration from spent sulfite liquor, alkaline epimerization of glucose or fructose, or other sources could be used as starting material for the production of mannose chemicals. This part of the investigation was carried out on a bench-scale using concentrated solutions. In many cases, massive crystallization of sodium mannose bisulfite occurred in a matter of minutes, following the addition of seed crystals. However, study of optimum crystallization conditions, with the objective of reducing occluded adducts from the other sugars, was not pursued to the same extent as in comparable work using spent sulfite liquor. Minor contaminants in the form of other sugar adducts were easily removed by recrystallization, which also proved successful in the removal of lignosulfonate contaminants from the product derived from spent sulfite liquor.

In the case where mannose polymers are the primary resource, it was shown that sulfurous acid hydrolysis was very effective, with the advantage that this reagent becomes part of the bisulfite chemical required to form the overall adduct mixture. In most cases a small excess of bisulfite reagent was used in reaction mixtures. Limited work was also carried out successfully, using potassium and ammonium bisulfite reagents as the basis for the separation of the mannose derivatives.

A number of uses or markets for sodium mannose bisulfite are suggested. In this study, the main objective was to use the derivative to produce pure mannose in commercial quantities. Sodium mannose bisulfite is very stable. In the form of a white crystalline powder it could be used as a chemical synthesis intermediate for the manufacture of medicinals, germicides and dyes where sulfite reagents are present. It could also be used as process additive in photographic and metal plating baths, and as a food preservative and carrier for sulfite reagents.

Methyl Mannoside

Glycosidation concurrent with methanolysis was found to be an efficient means for converting mannose polymers to monomeric glycosides. This was particularly true for the wood-prehydrolyzate raw material, where only 15 min of reaction time at 91°C was required for satisfactory hydrolysis. Methanolysis under reflux conditions (64°C) required several hours. The main disadvantage of this procedure is

the corrosive nature of the methanol-HCl reagent, which however was easily recovered for recycle, whereas a sulfuric acid glycosidation must be handled in a different manner. Purification of the crude sugar glycoside mixture was problematic at first because of interference from lignin-related contaminants. It was found that a changeover from methanol to water solvent, under carefully controlled conditions, following recovery of the glycosidation reagent (methanol-HCl), permitted separation of a water-insoluble fraction containing the principal colored contaminants. Subsequent minor decolorizing, using activated carbon resulted in clear, nearly colorless mixed methyl glycoside products, from which methyl mannoside could be crystallized in about 90% yield.

In order to be more certain regarding the recovered yield of methyl mannoside from the gross mixture, it was necessary to analyze the mixture for methyl mannoside content, since conversion of the raw material to glycosides was not always quantitative, and it was desired to study the recovery of product at each stage in the overall process. A gas chromatographic method [8] was used for this purpose. With this information it was possible to determine that methyl mannoside recovery from mixed glycosides can be carried out quantitatively, particularly if the material balance includes recycle of crystallization solvent or stage crystallization. The purity of methyl mannoside products obtained from crude materials was excellent and was improved to 99+% by easy, rapid recrystallization.

From an economic standpoint it was concluded that recovery and sale of a mixed methyl glycoside product for use in various resin manufacturing processes would be necessary. The main factors against the choice of the wood-sugar methyl glycoside route to mannose were: (1) the need to convert relatively dilute raw-material solutions to dry form prior to glycosidation; (2) the cost and corrosion problems of the reagent; (3) the more expensive pressure equipment required for rapid methanolysis; and (4) the more demanding hydrolysis reaction needed to regenerate mannose from methyl mannoside. It would be more favorable to sell methyl mannoside and the mixed methyl glycoside product than to regenerate mannose.

Uses and markets for methyl mannoside and the mixed methyl glycoside would include those already established for methyl glucoside as a polyol reagent in polyurethane, polyester and polyether resin manufacture. The stability of methyl glycosides is such that these intermediates are useful in a variety of syntheses to produce surfactants, emulsifiers, plasticizers, drying oils, varnishes and other surface coatings. General use is also suggested in the modification of urea-formaldehyde and melamine-aldehyde resins, hot melt adhesives and wax formulations.

Regeneration of Mannose from Sodium Mannose Bisulfite

Rapid, efficient procedures were developed to accomplish this objective, while also producing a useful sulfite chemical. The method of choice, involving a short-time exposure to mild alkaline conditions did not appreciably detract from the purity of the mannose product. The alkaline epimerization [18] of mannose to glucose and fructose was thus minimized while process economics were favored by the use of low-cost equipment, rapid processing and low-cost regenerating chemical. Neutralization of the slightly alkaline alcohol solution of mannose by using $CaCl_2$ was found very advantageous for precipitation of troublesome colored impurities. Methyl alcohol was also used successfully as the regeneration process solvent.

Other regenerating procedures, such as the use of calcium chloride, ion exchange resins, and electrodialysis, were tested and found successful, though probably not practical based on the economics of the use of $NaHCO_3$ or $NaOH$ as the alkaline reagent and recovery of solid sodium sulfite for recycle. Markets for mannose include use as a food material or additive and for production of mannitol, mannonic acid, sodium mannoheptonic acid and other mannose derivatives. Medicinal uses are also indicated, particularly as a dietary sugar to improve the retention of calcium and thus aid in bone ossification.

Sodium Mannoheptonate

Only the sodium-D-glycero-D-galactoheptonate isomer was found to be crystallizable from a crude mixture of the sodium salts of the aldonic acids generated when mixed-wood sugars or spent sulfite liquors were treated by the Kiliani procedure [19]. The observation that this sodium mannoheptonate isomer could be crystallized directly in 6–8% weight yield from a spent sulfite liquor reaction mixture was reported in 1965 by Boggs [20–22]. Four methods to separate sodium aldonates from the crude reaction mixture were described. From this work it may be concluded that at least the D-glycero-D-galacto-heptonate isomer, as illustrated in Figure 6, may be crystallized selectively from a variety of mixed monomeric wood-sugar resources following appropriate treatment with the NaCN reagent. In work carried out during the course of this investigation, the crystallization of the D-glycero-D-galacto isomer of sodium mannoheptonate from conifer spent sulfite liquor and prehydrolyzate raw materials was confirmed.

The sodium salts of aldonic acids are generally useful as additives in alkaline washing compounds, detergents, scale inhibitors, photographic processing compounds and phosphatizing agents. They are used in metal cleaning, derusting and alkaline treatment (etching), and as additives in metal electroplating baths. Aldonic acids form chelates with many metals and such derivatives are useful as medicinals and as agricultural micronutrients. In Portland cement concrete technology, the aldonic acids are the best set retarding additives for use in hot environments, to prolong the set in "exposed" aggregate surfaces, and to provide longer concrete placement and working time when needed for engineering or limited labor reasons.

Mannitol

The history of mannitol and the development of commercial processes for sorbitol, from which yields as high as 20% by weight of mannitol are obtainable, provided the earliest clues suggesting that other mannose derivatives might be crystallizable and different enough in solubility to permit separation from mixtures of other common monosaccharide derivatives of the same type.

As previously discussed, this mannose derivative is already an article of commerce. It is widely used as a solid dietetic sweetening agent and would probably have wider usage if it were cheaper. It is also used as a nonhygroscopic base or carrier for medicinals, as in the manufacture of pills, and in the synthesis of medicinals. Mannitol would be generally useful in the synthesis of polymer resins, drying oils, plasticizers and emulsifiers.

Economic Considerations

Two processes have been described, which provide routes for separating a mannose derivative from crude mixtures containing the same derivatives of other wood sugars and major contaminants. The derivatives obtained from the "bisulfite-adduct" and "methyl glycoside" processes could be used for regeneration of mannose. Two additional known processes (polyol and aldonic acid) have been discussed, which could be used to separate mannose derivatives from a mixture of the corresponding sugar derivatives. It would not be economic to regenerate mannose from mannitol and sodium mannoheptonate, because these products have higher value markets and applications based on their own chemical and physical properties.

The main features of the bisulfite-adduct and methyl-glycoside processes are summarized below.

Bisulfite Adduct Route:

1.   All process equipment is relatively simple and does not require the use of pressure vessels. Both batch and continuous operation are efficient.

2.   Raw materials should be concentrated to an appropriate value, such as 40–60% solids to obtain maximum efficiency and reduce equipment size. The raw material may be a complex mixture as in the case of spent sulfite liquor.

3.   Process chemicals are relatively inexpensive, noncorrosive and are mostly recycled to the process. Process solvent is recovered and recycled.

4.   The time at room or warm temperatures required to separate sodium mannose bisulfite crystals from the mixed sugar-bisulfite mixture is short, particularly when methanol or other alcohols are used to reduce the solubility of the product in the water-methanol solvent system.

5.   Product yield is nearly quantitative based on the mannose present in the raw material.

6.   The product is stable and is easily purified for sale as a dry crystalline powder.

7.   Mannose is rapidly and efficiently regenerated to produce a pure mannose syrup in very high yield. By-product sodium sulfite is recycled.

8.   In the case of the spent sulfite liquor raw material, the by-product liquor may be processed for heat and chemical recovery or used for the manufacture of modified lignin products for sale.

Methyl Glycoside Route:

1.   Reactor equipment must withstand the corrosive effects of acid reagents and would require design for operation under pressure to minimize reaction time. Other equipment, such as for filtration and solvent recovery, must withstand corrosion.

2.   Raw materials need to be provided in a dry form, but may be contaminated with noncarbohydrates.

3.   Process chemicals are relatively inexpensive. Methanol serves both as re-

agent and solvent.   The solvent portion and acid reagent (HCl) may be recovered and recycled.

4.   Crystallization of methyl mannoside is slower than in the bisulfite adduct process.

5.   Product yield is nearly quantitative based on product analysis in the methyl glycoside mixture.   The by-product syrup of mixed methyl glycosides is also valuable and could be marketed.

6.   Methyl mannoside is a stable compound and is easily purified for sale as a dry crystalline product.

7.   Although mannose is easily regenerated from methyl mannoside by acid hydrolysis, the final step is definitely not economic if mannose is the primary product.

If the above features are used as the assumptions in cost calculations, the production of mannose and mannose chemicals via the sodium mannose bisulfite route is considered to be the most attractive from an economic standpoint.   The methyl glycoside route is economically attractive only in the case where both methyl mannoside and mixed methyl glycoside products are marketed as such and when the raw material is already available in a low-cost dry form as would be possible when using wood prehydrolyzates (spray-dried Masonex) and various dry mannose carbohydrate resources (seaweeds, coniferous hemicelluloses such as glucomannans, galactoglucomannans).

CONCLUSION

Four mannose derivatives are now known to have solubility and crystallization properties that permit commercial separation from mixed monosaccharide derivatives of the same type.   It has been shown that the bisulfite adduct separation route is rapid and inexpensive and is also the most favorable for regeneration of mannose.   The methyl glycoside route could be used advantageously for converting dry polymer raw materials to industrial glycoside products.

Contribution No. 143 from the Research Divisions of ITT Rayonier Inc.

REFERENCES

[1] J. K. Hamilton, *Pure Appl. Chem., 5*, 197 (1962).

[2] R. L. Casebier, J. K. Hamilton, and H. L. Hergert, *Tappi, 52* (12) 2369–77 (1969).

[3] K. D. Sears, A. Beelik, R. L. Casebier, R. J. Engen, J. K. Hamilton, and H. L. Hergert, *J. Polym. Sci. C, 36,* 425–433 (1971).

[4] J. E. Jeffery, E. V. Partlow, and W. J. Polglase, *Anal. Chem., 32* (13), 1774–77 (1960).

[5] R. L. Casebier, F. W. Herrick, K. R. Gray, and F. A. Johnston, U.S. Patent 3,677,818 to ITT (1972).

[6] J. K. Hamilton, F. W. Herrick, and J. D. Wilson, U.S. Patent 3,507,853, to ITT Rayonier (1970).

[7] J. K. Hamilton, F. W. Herrick, and J. D. Wilson, U.S. Patent 3,531,461 to ITT Rayonier (1970).

[8] H. E. Brower, J. E. Jeffery, and M. W. Folsom, *Anal. Chem., 38,* 362–64 (1966).

[9] R. Hilf and F. F. Castano, *Anal. Chem., 30,* 1538 (1958).

[10] W. Pigman (Ed.), *The Carbohydrates,* Academic Press Inc., New York, 1957, pp. 249–250.

[11] R. J. Wicker, *Chem. Ind. (London),* 1708–16 (1966).

[12] M. Proust, *Ann. Chem. Phys., 57* (1), 144 (1806).

[13] H. J. Creighton, *Can. Chem. Process Ind., 26,* 690–6 (1942).

[14] R. A. Hales, U.S. Patent 2,289,189 to Atlas Powder Co. (1942).

[15] L. Kasehagen and M. M. Luskin, U.S. Patent 2,759,024 to Atlas Powder Co. (1956).

[16] L. A. Boggs, Preprint, 155th National ACS Meeting, San Francisco, March 31, April 5 (1968).

[17] D. L. Ingles, *Australian J. Chem.,* 288–95 (1959).

[18] J. C. Speck, M. L. Wolfrom, Ed., in *Advances in Carbohydrate Chemistry,* Academic Press, New York, 1958 Vol. 13, pp. 63–103.

[19] E. Fischer and F. Passmore, *Chem. Ber., 23,* 2226 (1890).

[20] L. A. Boggs, Abstracts of Papers, 150th National ACS Meeting, Atlantic City, N.J. (1965).

[21] L. A. Boggs, Tappi, *50* (6), 133–135A (1957).

[22] L. A. Boggs, Can. Patent 811,048 to Pulp Manuf. Research League (1969).

THE LIGNOSULFONATE CHALLENGE

WILLIAM C. BROWNING

SCT Associates, Houston, Texas 77024

SYNOPSIS

Lignosulfonates are presented as heterodisperse nonlinear macromolecular polyelectrolytes existing in solution as prolate spheroids of low axial ratio with functional groups active at the surface. The colloidal properties of lignosulfonates are primarily responsible for surface active industrial applications. The ability of lignosulfonates to deflocculate solids dispersed in aqueous media contaminated with electrolytes is deduced from available data to be due to structurized multilayer adsorption. The relation of colloidal properties to performance is shown with particular reference to emulsification, deflocculation, chelation, adsorption, and use applications such as microencapsulation and drilling fluid additives. Specific chemical modifications used to enhance the performance of lignosulfonate functional chemicals are indicated. Examples of management sponsorship of stream pollution abatement and renewable resource utilization through innovative marketing, research, and development, are given. Future opportunities for increased use of lignosulfonates as functional chemicals are appraised.

INTRODUCTION

Lignin in sulfonated form has been available as an industrial raw material since 1886. Since about 1922 the pulp and paper industry has been concerned with its waste and highly pollution conscious [1]. Diligent study and effort to utilize spent sulfite liquors has continued for the past fifty years. The production of about 3,000,000 ton/yr of spent sulfite-liquor solids in solutions of about 10% concentration and the lack of available volume markets for the product has been a continuing frustrating problem.

Purified lignosulfonates have been commercially available since the early 1930s. These lignosulfonates are unique and multifunctional macromolecular polyelectrolytes. Lignins and lignosulfonates are recognized feedstocks for the manufacture of low molecular weight aromatic chemicals. Among these commercially available are vanillin, dimethyl sulfide, dimethyl sulfoxide, methyl mercaptan, catechol, etc.

Lignins have been the subject of sustained worldwide research for about a century. The technical literature is voluminous. More than 3,000 patents have been issued concerning potentially useful lignin derived products and processes of man-

ufacture. Despite of all this, only about 20% of the lignosulfonates produced in the U.S. are processed for industrial use [2].

This anomaly of a versatile chemical raw material of proven value and usefulness being dumped as a waste and in general constituting (as a pollutant) an expense item, instead of significantly contributing to the betterment of society and the gross national product, is the "Lignosulfonate Challenge."

Because of the pressure to dispose daily of large tonnages of by-product sulfonated lignin produced by the sulfite pulping of wood, the utilization of spent sulfite-liquor solids has tended to be regarded primarily as a waste-disposal problem instead of a challenge to optimize the use of a renewable resource. The policy of encouraging volume sales essentially for pollution-control purposes has fostered unrealistic low-cost commodity pricing and price-war tactics. As an additional result, the prospect of a low rate of return on product sales has discouraged the funding of application research and capital allocation for new product development. Positive incentive to meeting the lignosulfonate challenge may be provided by increasing the attention given to the design and marketing of noncommodity lignosulfonate specialty products.

The colloidal properties of lignosulfonates have been primarily responsible for their usefulness in industry. The understanding of the relationship of these properties to performance is fundamental to applications research and market development.

The purpose of this paper is to place in perspective what beginnings have been made toward meeting the lignosulfonate challenge. Illustrative examples will be given of forward-looking management action, innovative application research and aggressive market development. This perspective will be presented from an industrial viewpoint based upon industrial research and marketing experience.

To avoid redundancy and condense the explanatory technical information given to illustrate the developing interdisciplinary aspects of colloid-related lignosulfonate technology, a number of references are cited. However, no attempt is made to review the lignin literature or to present a consensus. Space necessitates that this discussion be incomplete in many respects. It is recognized that the contributions to lignosulfonate technology made by many countries are numerous and important. Nevertheless, to keep the discussion within reasonable limits, only U.S. products and processes will be used as examples or discussed.

PURIFIED LIGNOSULFONATES

To optimize the effectiveness of lignosulfonates, they should be substantially freed from wood carbohydrates. Such carbohydrates not only dilute the lignosulfonate, they also inhibit desired surface active properties.

Spent sulfite liquors (SSL) are approximately 10% solutions of a mixture of lignosulfonates and carbohydrates. In softwoods, the lignosulfonates constitute about 55% and carbohydrates about 32% of the liquor solids. For hardwood liquors the proportions are about 42% lignosulfonates and about 45% carbohydrates. Clearly, the profitable use of SSL must include use of both lignosulfonates and carbohydrates.

Much can be learned concerning management as well as technology from the first commercial operation for the preparation of purified lignosulfonates as instituted at Rothschild, Wisconsin. D. C. Everest, Vice President and General Man-

ager of Marathon Paper Mills (later President of Marathon Corporation), recognized in the mid-1920s the growing national importance of stream pollution and the desirability of converting SSL into products of value. Acting upon this perception, Guy C. Howard was engaged to put into operation his lime precipitation process for removal of lignosulfonates from SSL. The faith of D. C. Everest was subsequently justified and the Rothschild lignosulfonate operation is now a profitable segment of the American Can Company.

The original work at Rothschild was conducted under the direction of Guy C. Howard. He considered his process to have two objectives: (1) provide an economical means of treating SSL to "avoid objections raised to their discharge into streams and to recover products for use at the pulp mill in making fresh cooking acid and as a boiler fuel"; and (2) "provide supplemental processes for making special products." These special products were purified and modified lignosulfonates [3].

Based on pilot plant work and prior to the construction of a commercial plant, the decision was made "to investigate the recovered organic products for more profitable uses than as a boiler fuel, and to study the tail-out effluent (carbohydrates) as regards recovery of additional commercial products . . ." [4].

After commercial operations were underway it was noted that although supplemental processes for making special products were developed, "the markets for such products are not unlimited . . .."

Howard further advised that insofar as stream pollution control was concerned, the pulp mill should use the recovered products for making fresh cooking acid and boiler fuel rather than being dependent on outside markets. This is still sound advice.

In most chemical manufacturing operations, raw materials are used as required. Variations in production output and sales due to varying demand is regarded as normal. If an SSL chemical operation is the sole means of controlling stream pollution, then seasonal slumps in sales or any variation resulting in less than complete processing of SSL cannot be tolerated—obviously not a realistic business concept. Under the Howard concept, as more profitable uses for lignosulfonates are developed, less will be used as fuel but normal production fluctuations can be accommodated without jeopardizing stream pollution control.

Studies were continued at Rothschild concerning the "supplemental processes" of Howard. New materials and new applications were developed [5]. It is noteworthy that sales development occurred because of market development. Markets were created by probing specialty chemical application technologies for problems that might be solved by the application of modified lignosulfonates [6]. A small but active and knowledgeable sales staff not only suggested possible applications to the trade industries but sought out technical problems and relayed them to Rothschild for study and analysis. Technical information concerning not merely product analysis but colloid mechanisms and functional properties were distributed to stimulate customer interest in lignosulfonates and their use.

These techniques greatly assisted in developing applications for purified lignosulfonates. By the 1950s, a well-developed line of products with established markets necessitated the purchase of outside SSL to supplement the Rothschild SSL [7]. Although at present the Howard Process is used only on occasion and no SSL is used for fuel, the purchase of outside SSL is still necessary for the manufacture of the "special products" envisioned by Howard.

COLLOIDAL PROPERTIES

The established industrial uses of purified lignosulfonates are predominately in the realm of colloid science. Colloid science may be defined as the science of large molecules, small particles, surfaces, and the forces that govern their interactions. Colloid science thus becomes the common denominator for a wide range of industrial technologies, including such diverse fields as paper coatings, portland cement, textile processing, preparation of foods, and oil well drilling fluids.

In common with other colloidal and polymeric materials little systematic attention has been accorded the colloid chemistry of lignosulfonates [8]. A few limited investigations have been published concerning the effect of lignosulfonates upon the stability and rheology of suspensions as related to adsorption and molecular weight [9–11]. In drawing generalized conclusions from well conducted but specific experiments, one is well advised to give heed to the "blind men and the elephant" fable cited by Pearl concerning lignin concepts [12].

One capsule account of the surface active and colloidal properties of industrial purified lignosulfonates points out that commercial lignosulfonates are not only heterodisperse with respect to molecular weight but also consist of moieties of different molecular structure [13]. Therefore, industrial development must consider commercial lignosulfonates as a statistical entity, not as a classical chemical compound.

In the mid-1940s serious study of the colloidal properties of Howard Process lignosulfonates was instituted by the Rothschild group under the direction of J. R. Salvesen. At that time, little was known of the colloid mechanisms responsible for the industrial applications of purified lignosulfonates. It was recognized, however, that if new markets were to be developed or improvement in performance was to be achieved, more must be known concerning the colloid chemistry of lignosulfonates. It was conceded that utilization efforts should be oriented toward applications in which the unique properties of lignosulfonates were emphasized and that promotion of their use as "cheap substitutes" should be avoided.

Emulsification

In the early 1930s, samples of Howard's "special products" were submitted to a prestigious midwestern research institute to be evaluated as emulsifiers. After investigation, it was reported that the lignosulfonates had little or no value as emulsifiers. This expert opinion report, based upon drop-number experiments, discouraged early study of lignosulfonates as emulsifiers.

With the organization of colloid research at Rothschild, the subject of emulsion technology was reopened. It was found that lignosulfonates were exceptional oil-in-water emulsion stabilizers. At that point, the conventional methods of evaluating emulsion stability were resistance to electrolytes and centrifugation. These methods were found to be inapplicable to the lignosulfonate studies because lignosulfonates were capable of stabilizing emulsions in saturated salt solutions, were improved when subjected to shear, and were also stable to centrifugation.

Some of the information accumulated in these studies was summarized in a published paper directed toward possible application in oil well drilling fluids [14]. The principles discussed were put into practice three years later, increasing the usage of lignosulfonates in drilling fluids several fold and materially contributing to a multimillion-dollar lignosulfonate application.

Consistent with the developments in emulsion technology, other colloidal studies revealed that lignosulfonates could adsorb so strongly upon some surfaces that a three dimensional protective layer could be formed. These principles were developed into microencapsulation techniques in which free-flowing powders of liquid-in-solid or solid-in-solid dispersions could be prepared with lignosulfonates as the continuous phase. These encapsulation techniques were employed to prepare powders which when introduced into water formed "instant" emulsions of liquids, or dispersions of low melting solids. Commercial application of this microencapsulation technique were embodied in patents relating to the reinforcing of synthetic elastomers [15] and oil well drilling additives [16].

The use of lignin-derived products for the microencapsulation of materials in the areas of pesticides, agriculture, mariculture, and construction, is an intriguing potential volume market.

Deflocculation

The ability to disperse (deflocculate) or effect the colloidal stabilization of suspensions of solids is a property most commonly associated with commercial lignosulfonates. This so-called dispersant action and the use of lignosulfonates as "dispersing agents" or "dispersants" has wide industrial application as commonly listed in the product bulletins of the various suppliers of lignosulfonates.

In the mid-1940s, the efficiency of various Howard Process lignosulfonates as dispersants for various pigments and high surface-area powders was investigated including suspensions of kaolin, calcium carbonate, sulfur, titanium dioxide, zinc oxide, iron oxide [17], and carbon blacks [18].

One of the activities of the Rothschild colloid group was the study of the mechanism of colloidal stabilization by lignosulfonates. In these studies, a variety of techniques were employed for a number of years with numerous substances and disperse systems. Among the investigative methods used were microelectrophoresis, surface tension, interfacial tension, microscopy, ultramicroscopy, adsorption, diffusion, ultrafiltration, rheology of concentrated solutions, dilute solution viscometry, and an assortment of performance tests.

The electrokinetic theory of the stability of colloidal dispersions proposed by Hardy in 1900, confirmed by Burton in 1906, and extended by Powis in 1915, has had a continuing effect on the thinking of colloid chemists [19]. The electrokinetic theory of the stability of lyophobic colloids was treated in detail and mathematical relationships derived by Verwey and Overbeek [20]. The double layer concept of mutual repulsion of charged particles of like charge is easy to comprehend. As a result, this stabilizing mechanism is commonly presented in the trade and technical literature to describe the action of dispersing agents.

The mechanism of clay deflocculation was studied by Johnson and Norton [21]. They interpreted deflocculation in terms of the classical coulombic attractive forces and double-layer repulsion. Complete deflocculation was regarded to be possible only when hydroxyl ions were present in the water surrounding the dispersed particles and when the positive ion was monovalent and preferably sodium. Divalent ions such as calcium were regarded as acting to bind two clay particles together.

Following these concepts, Asdell [22] explained the deflocculating mechanism of dispersants on the basis of sequestration or precipitation of calcium, magnesium

or polyvalent ions by the dispersant. As is typical of conclusions derived from one set of experiments, the electrokinetic stabilization concepts proposed by Norton and Johnson, Asdell, and others, did not explain the rather extensive existing use of calcium lignosulfonates as dispersants or "water reducers" in portland cement technology [23, 24].

The developing colloid studies at Rothschild gave increasing evidence that the prevalent double layer electrokinetic concepts did not adequately account for all observed experimental results. It was also found that ultrafine calcium carbonate could be deflocculated by calcium lignosulfonate in the absence of sodium hydroxide or any sodium ions.

It was found by direct microscopic observation and by rheological properties that aqueous clay suspensions could be deflocculated by calcium lignosulfonate in the presence of 300 ppm or more calcium ions and in the absence of sodium or other monovalent ions. It was subsequently discovered that clays could be deflocculated in solutions of electrolytes including 6% sodium chloride [25].

The commercial use of lignosulfonates in gypsum wallboard, kiln feeds, pesticides, industrial cleaners, ceramics, and oil well drilling fluids, all involve the ability of lignosulfonates to act as deflocculants in the presence of contaminating electrolytes.

Evidence accumulated over the last three decades from the laboratory and from industrial usage show that lignosulfonates function to effect the colloidal stabilization of disperse systems in two ways:

1. Electrokinetic stabilization according to the concepts set forth by Verwey and Overbeek.

2. Steric stabilization, in the manner presented by Rehbinder [26].

Fundamental to both stabilization mechanisms were colloid studies conducted at Rothschild. These studies included (1) electroviscous properties of dilute solutions of lignosulfonates, (2) electrophoresis of lignosulfonate solutions, (3) viscosity-concentration relationships of lignosulfonate solutions, and (4) rheology of lignosulfonate solutions of 20 to 35% concentrations.

The discovery that lignosulfonate solutions of high concentrations behaved as Newtonian fluids was of great significance in confirming dispersion stabilization mechanisms [27].

Rehbinder, who has devoted considerable effort to the study of concentrated dispersed systems, believes that effective stabilizing action by the adsorbed layer is possible if the layer is structured; i.e., it has a much higher viscosity than the medium and thus serves as a mechanical barrier to prevent particles in normal Brownian movement from approaching each other within the critical range of attraction.

The globular nature of the lignosulfonate molecule does not fit the concept of entropy stabilization as developed by van der Waarden [28]. Calculations made by Vold [29], however, are relevant as are the contributions of Heller [30].

The concept of steric stabilization by condensed-layer adsorption (structured or multilayer adsorption) tends to be overlooked in technical or trade literature, even though it provides a mechanism for deflocculation in the presence of strong electrolytes or in apolar media.

Lignosulfonates differ in their protective action from the classical protective colloids in that they do not bind or immobilize quantities of the solvent media as do gums and starches. Using lignosulfonates, stabilized suspensions of high solids

concentration and low viscosity may be prepared, even in the presence of contaminating electrolytes. This is something that cannot be done with classical electrokinetic or protective colloid stabilizers.

Lignosulfonate colloid data are in accord with the Rehbinder concepts. It should be noted that electrokinetic stabilization requires only monolayer adsorption and about 0.2% dispersant on the weight of the disperse phase. Excesses of dispersant will cause destabilization. The ionic nature of the dispersant itself in the media can cause compression and collapse of the double layer. Structurized stabilization requires a concentration of dispersant in the medium sufficient to cause multilayer adsorption. In dispersions of high solids content this usually is about 5-6% on the weight of the dispersed solids. With this mechanism no destabilization effects occur because of excess of dispersant.

The available physical evidence indicates that the nature of lignosulfonates enables both stabilizing mechanisms to be operative at concentrations of contaminating electrolytes that would render the classical electrokinetic type of dispersing agent inoperative because of collapse of the double layer. This dual stabilizing property has been primarily responsible for the application of lignosulfonates in oil well drilling fluids [31].

Chelation

Any organic compound containing intramolecular hydrogen bonds will, in general, react with divalent or multivalent metal ions to form covalent coordinate bonds. Coordination can occur with organic compounds containing the necessary donor groups in the proper position. Such donor groups include —OH, COOH, and $=O$ in ortho or para positions to each other. The presence of donor groups necessary for the formation of chelate configurations has been amply demonstrated in lignin structure research.

It was early noted at Rothschild that in preparing lignosulfonic acid salts by double decomposition (metathetical) reactions, that greater amounts of chemically combined metals (such as iron, copper, or zinc) could be obtained than could be stoichiometrically accounted for on the basis of sulfonic group content. The ability of Howard Process lignosulfonates to chelate calcium was utilized in the late 1930s in commercial compositions to prevent the efflorescence of calcium sulfate on structural ceramic wares. Other industrial uses of the chelating properties of commercial lignosulfonates has been cited by Pearl [32] and by Hoyt and Goheen [33]. The prediction by Guy Howard that purified lignosulfonates would find application in agriculture has been realized in the use of lignosulfonate chelates as trace element or micronutrient compounds.

The chelating properties of lignosulfonates has been used to facilitate the cross-linking of polysaccharides in nonclay type of drilling fluids [34,35].

It appears that the chemistry of lignosulfonate coordination compounds is an important facet of lignosulfonate utilization and affords considerable development potential.

Adsorption

The industrial uses of lignosulfonates in many applications including emulsion stabilization, deflocculation, elastomer reinforcement, adhesives and water treating (boiler scale control) is fundamentally dependent upon adsorption phenomena. The literature concerning polyelectrolyte adsorption is meager and inconclusive.

No comprehensive study concerning lignosulfonate adsorption has yet been made, although several limited studies of lignosulfonate adsorption have been published. Conclusions based upon dilute solution adsorption should be tested against established use practices and are advisably evaluated with the previously mentioned elephant fable kept in mind.

Although the concept of multilayer adsorption in liquid-solid systems is frequently questioned, multilayer and condensed layer adsorption is readily accepted in gas-solid systems. This may be because studies of polyelectrolyte adsorption including lignosulfonates have been concerned with adsorption from relatively dilute solutions. Studies with gases, on the other hand, in addition to having amenable rates of adsorption, have frequently involved measurements at increased pressures which are tantamount to increasing the concentration of the gas molecules.

The common experience of deflocculating a slurry with a low concentration of lignosulfonate (ca. 0.2% on solids), then destabilizing with added electrolyte (NaCl, $CaSO_4$), and finally restabilizing the dispersion by increasing the concentration of lignosulfonate (ca. 5.0% on solids), is difficult to explain on the basis of monomolecular adsorption and double layer stabilization. The structurized layer concept of stabilization invokes multilayer adsorption. Other workers have compared experimental results and concluded that the complete restriction of macromolecular adsorbtion to a monolayer concept is not justified. A broader-based theory of macromolecular adsorption based upon experimentally verified multilayer adsorption has been advocated [36].

Colloid studies have indicated that lignosulfonate adsorption, as exemplified by the Howard Process products, was dominated by hydrogen bonding mechanisms. The carboxyl, carbonyl, aliphatic and phenolic hydroxyl groups of the lignosulfonate moieties are all proton donors. Phenolic hydroxy groups in particular are strongly hydrogen bonding. Completely methylated lignosulfonates were found to be inactive as dispersants. Demethylation of the lignosulfonates was found to increase their adsorbability and dispersant capability.

Nonpolar Van der Waals' forces also play a part in adsorption and increase in strength with increasing molecular weight.

The sulfonic group, normally considered as the dissociating group providing a strong double-layer charge effect, is capable of forming a covalent bond with alumina surfaces, whereas only —OH bonding occurs on silica surfaces. Thus sodium lignosulfonate is an efficient deflocculant for kaolin clays which have both an alumina (gibbsite) surface and a silica surface in their crystal structure. Sodium lignosulfonates, unless modified, are only mediocre dispersants for montmorillonite and illite which are characterized by a plate-like crystal structure having two silica surfaces. Polyphenolic macromolecules, such as quebracho, are strongly adsorbed on silica surfaces via hydrogen bonding.

The structures present in lignosulfonates capable of forming chelates are also capable of strong adsorption at some solid-liquid interfaces by forming surface complexes with the solid.

Strong adsorption bonding by lignosulfonates and their ability to coordinate with some inorganic crystal lattices act to modify crystal habit during crystallization from solution. This property is used industrially in a number of applications including water treatment and boiler scale control. Crystal-habit modification is not to be confused with sequestration or threshold effects [37].

Experimental evidence indicates that lignosulfonate adsorption may be effected by one or more of the following:

1. nonpolar Van der Waals' attraction
2. hydrogen bonding
3. covalent bonding
4. ion exchange

Adsorption of a solute at a solid-liquid interface may be regarded as the result of competition for the solute between the liquid media and the solid substrate. Lignosulfonates behave in a manner common to polyelectrolytes. Higher molecular weight polymers are, in general, less soluble than low molecular weight polymers and thus tend to be more highly adsorbed. This may be reversed if the lower molecular weight material has more hydrogen bonding groups or other bonding structures, or if the higher molecular weight material has more solubilizing groups.

Introducing an electrolyte salt into the aqueous dispersion media will render a polyelectrolyte solute less soluble and will therefore cause an increase in adsorption, unless the electrolyte blocks adsorbtive sites on the solid phase substrate. This effect, in general, persists up to the point the solute precipitates or "salts out." At this point, introduction of solubilizing agents such as NaOH will again render the solute capable of adsorption. In the absence of a contaminating electrolyte, the addition of sodium hydroxide may increase the solubility of the lignosulfonate to limit sorption or even cause desorption of the lignosulfonate.

The absence of oil soluble groups in the structure of lignosulfonates cause them to be readily desorbed or replaced at an oil-water interface by a chain-structure surfactant having an oil-soluble chain component. Although strongly hydrophilic, the lignosulfonates exhibit no expanding coil or water-imbibing properties as do, respectively, polyacrylates and starch.

The study of adsorption from aqueous solution of macromolecular, heterodisperse polyelectrolytes, such as commercial lignosulfonates, is complex. To derive valid conclusions, factors such as the nature of the solid substrate, the molecular structure of the polyelectrolyte, the pH and electrolyte content of the aqueous phase, temperature, time and concentration, must be evaluated as a variable and mutually interdependent relationship.

CHEMICAL MODIFICATION

Lignin contains a variety of functional sites and is capable of undergoing a variety of modifying reactions. These organic chemical reactions have been summarized [32, chap. 6; 33, chap. 13]. This information is largely derived from studies concerning the genesis of lignin and studies relating to the sulfite pulping process. The patent literature is replete with references to chemical modifications made to achieve empirical performance characteristics. On the other hand, the literature relating the specific and selective modification of colloidal properties by chemical reactions is quite sparse.

The following examples of chemical modifications of commodity calcium and sodium lignosulfonates are drawn from those products that have been commercially produced and sold in significant quantities.

One of the early applications of colloid chemistry was the development in 1946 of a carbon-black dispersant by desulfonating lignosulfonates and by treatment to

create an abundance of phenolic hydrogen bonding groups [38]. Thus modified, the lignosulfonate derived material became an effective general dispersant and found application in dyestuff technology. This modification and related compounds are still actively being used as commercial dispersants and water-treating compounds.

Lime treated oil well drilling muds were developed in the 1940s to provide better borehole protection, temperature stability and resistance to contaminating electrolytes than the then current phosphate and sodium tannate treated muds. Calcium lignosulfonate was found to be a "thinner" for such muds. A lime condensed sodium-calcium modified compound of selected molecular weight was developed that performed in a markedly superior manner to common commodity calcium lignosulfonates [39]. Also based on colloid property considerations, a lime condensed sodium lignosulfonate was specifically developed to be used in saturated sodium chloride drilling fluids [40].

Utilizing the covalent bonding of aluminum for clay surfaces, the hydrogen-bonding propensity of hydrous aluminum oxides and the ability of lignosulfonates to form chelates, an aluminum lignosulfonate complex compound was developed as a drilling fluid additive [41]. This compound was designed to be effective without the necessity of adding lime or any other electrolyte. It would, however, stabilize the mud in the presence of cement, salt, or gypsum contamination. In addition, the drilling muds treated with the aluminum complex compound were much more temperature resistant than lime treated drilling muds. However, like the chromium lignosulfonate products, this aluminum containing compound required the use of sodium hydroxide for activation. Sodium hydroxide-treated high pH drilling fluids are now regarded as undesirable from the standpoint of formation damage and borehole destabilization [42].

The improvement in dispersing action of sulfite liquors by treatment with oxidizing agents including chromic acid and permanganates was demonstrated at an early date [43]. As early as 1910 it was recorded by Philippi that the dispersing properties of lignosulfonates were increased by treatment with chromium salts which form hydroxides when made alkaline, or by treatment with chromic acid or chromates which reduce to trivalent chromium salts that can form hydroxides [44].

The application of oxidation and chromate treatments to lignosulfonates for the purpose of preparing drilling fluid additives was shown by Byrd [45].

The adaptation of techniques involving the use of oxidizing agents such as chromates and the preparation of lignosulfonate compounds containing aluminum, iron, copper and chromium as drilling fluid additives, was made by King and his co-workers [46]. The King et al. patents issued in 1960 contain a rather comprehensive discussion of known methods of effecting changes in the colloid chemistry of lignosulfonate, e.g., acid condensation, alkaline hydrolysis, etc.

Subsequently these workers obtained numerous patents in which oxidized and chromium, iron, copper, and aluminum containing lignin derived materials were proposed as improved products for use in a wide variety of applications in which sodium or calcium lignosulfonates had established their usefulness.

The chemical changes induced by treating lignosulfonates with chromium containing salts have direct effect on the colloidal properties of the resulting compounds. Dichromate oxidation has been shown to effect demethylation and promote the formation of catechol and pyrocatechol groups—reactions that would in-

crease the adsorbability of the lignosulfonate by hydrogen bonding mechanisms [47,48].

The trivalent chromium formed by the reduction of hexavalent chromium compounds is available to form chromium sulfonate lignin salts by double decomposition if circumstances permit. Chromium hydrous oxides would form when the solutions of trivalent chromium lignosulfonate salts were made alkaline and thereby increase the dispersive effectiveness of the lignosulfonate as shown by Philippi. In addition, the crosslinking effect caused by dichromate treatment acts to increase effective particle weight and solution viscosity which, as previously indicated, can increase the effectiveness of dispersing action by condensed layer stabilization.

The use of chromium sulfate in conjunction with sodium lignosulfonate without oxidation has been used to formulate a drilling fluid additive [49]. In this instance, the native ability of the lignosulfonate to scavenge oxygen was retained for corrosion control purposes. In this process, the nongelling action of trivalent chromium salts as noted by Tenaka and Senju was deliberately utilized to simplify manufacturing operations [50].

Lignosulfonates treated with formaldehyde and ammonia to increase adsorption and solution viscosity have been used to chelate chromium for the purpose of forming a multipurpose nondispersing drilling fluid additive [51,52]. Phenol formaldehyde treated lignosulfonates have been used to increase adsorption by hydrogen bonding and molecular weight increase to improve dispersant action and also to prepare adhesives.

Hydrolysis reactions to increase phenolic groups have been used to increase the chelating efficiency of lignosulfonates and improve their performance as micronutrient compounds for agricultural use.

To date, a seeming myriad of lignosulfonate reaction products have been investigated and patented. Included among these are reactions with furfural, proteins, polyisocyanates, graft polymerization with acrylates, methylmethacrylates, styrene, etc. The variety of functional sites and the various reaction capabilities of lignosulfonates strongly suggest that there are many known ways in which modification procedures could now be employed to convert lignosulfonates into more desirable products for specific uses.

The increasing realization of the imperative necessity for the use of renewable resources should stimulate management consideration of the further use and development of forest industry products.

MARKETING, RESEARCH, AND DEVELOPMENT

The vast unused array of proposed lignosulfonate products and uses for lignosulfonates recorded in the literature is ample evidence that more is required than research and patents to achieve the profitable industrial use of lignosulfonates. In the industrial environment, it cannot be assumed that a product will sell simply because it is good and performs well.

The experience of development and marketing of new products as recorded in trade publications indicates that classical management techniques are frequently inadequate, because they do not cope with marketing complexity, risk, and uncertainty; are not responsive to marketing needs and high degree of program change; are not flexible or predictive; and do not involve the organizational interdependen-

cies that exist in a marketing program [53]. It is indicated that future progress in the utilization of lignosulfonates will be dependent upon making use of the best available management techniques applicable to new product development and marketing [54]. Basic and fundamental to any successful development effort is long-range planning, commitment and sponsorship by top management.

The attitudes toward spent sulfite liquors may be summarized as follows:

1. Simple disposal to eliminate stream pollution, e.g., ponding, deep-well injection, or dumping at sea.

2. Dispose of SSL in a manner that pays for the disposal operation and possibly makes a profit.

    a. With minimum of processing and organizational effort, e.g., burning, use as road binder, linoleum paste, molasses diluent, etc.

    b. With significant processing and organizational effort develop a stabilized volume marketing operation, e.g., supply on a commodity basis desugared lignosulfonates for cement additives, industrial binders, dispersants, etc.

3. Contribute to the long range national economy by considering SSL as a renewable resource and processing, possibly in a sophisticated manner, to maximize return on investment even with a low tonnage output; e.g., use of carbohydrates to produce protein, use of lignosulfonate to produce fine chemicals (vanillin, DMSO, catechol), and use of the sulfonated lignin polymers as specialty (functional) chemicals (carbon black and dye dispersants, drilling fluid additives, boiler water treating chemicals, etc.).

It is desirable to take advantage of the economical source of sulfonated polymers in SSL to develop functional chemicals.

Functional chemicals (or specialty chemicals) are defined as those chemicals closely related to or identified in terms of use or function. Functional chemicals may be the minor component of a total formulation but contribute significant and unique properties to the product. Functional chemicals are sold not to composition or chemical analysis specifications, but to specifications of performance. The pricing of functional chemicals is usually based on the value to the customer, whereas commodity chemicals are priced relatively low and are usually based on manufacturing cost. Functional chemicals characteristically have high return on investment (ROI) and high return on sales (ROS).

It should be well noted that the usage of chrome-treated lignosulfonates in drilling fluids is not because they are a lower-cost alternative product, but because they have unique properties not available in other products.

Unfortunately, even modified lignosulfonates have traditionally been marketed as pseudocommodities. Pseudocommodities, unlike true commodities, are produced not to composition specifications, but to specifications of performance and are priced as are commodities. The low ROI and ROS status of lignosulfonate marketing has, quite naturally, had a low stimulus value to top management. It is recognized that some pseudocommodity marketing may always be desirable for economic and manufacturing reasons. However, pseudochemical sales for pollution control purposes should not be allowed to force marketing decisions not in the best interests of profitable chemical product development.

The evolving energy situation has increased the attractiveness of lignosulfonates as a fuel. Burning is the complete disposal mechanism not dependent upon outside markets. The use of lignosulfonates as a fuel should be regarded as an intermediate step, not the ultimate objective.

The fuel value of the lignin material becomes the economic base line for chemical production. All new products, therefore, must have a profit contribution in excess of fuel value to be favorably considered. This is in accord with the use of petroleum which has been referred to by many, including the Shah of Iran as being "too valuble to burn" [55].

The economic potential for functional chemical product development is positive. It has been estimated that pseudocommodities had a value of 14 billion dollars in 1973 and are projected to be 27 billion (in 1973 dollars) in 1985. Specialty chemicals were estimated as 10 billion dollars in 1973 with a value of 25 billion (in 1973 dollars) projected for 1985 [56]. It has been projected that specialty chemicals will increase by about 12% per year during the oncoming decade and continue to return 15-20% or more on capital invested.

The opportunities for the development of lignosulfonate functional chemicals are numerous but not likely to be determined by conventional market surveys. Future potentials will result from exploiting the inherent properties of lignosulfonates and their modifications to create new markets.

Market creation is not an impossible procedure. Xerox had to create a market for its unique copying process and in so doing grew from a $2,000,000 sales operation to a $150,000,000-plus operation in ten years. For that matter, Henry Ford did not initiate his operation on the basis of an existing market but on the belief that his product would create its own market.

The use of lignosulfonates in drilling muds was a nominal 15,000 ton/yr in 1956-1959. Exploitation of certain inherent properties of lignosulfonates as modified by treatment with chromium compounds was initiated by Milchem Incorporated. This directly resulted in increasing the total industry usage of lignosulfonates to more than 90,000 ton/yr by 1965. This increase did not occur just because of a special compound, a technology of modifying lignosulfonates, or innovative changes in drilling fluid practice. All of these factors played a part, but all had been available to the drilling industry for several prior years. The creation of this expanded market made by coupling quality products with improved technology and service was the work of an aggressive marketing force. Thus, one company by the success of its marketing efforts led competititors and the industry to adopt and adapt new engineering techniques which resulted in multiplying the total drilling fluid usage of lignosulfonate products six- to sevenfold.

An untapped area of market development for the wood chemicals industry is the providing of formulated specialty chemicals to various specialty sales organizations. The manufacture of formulated compositions should be given serious consideration as a highly profitable activity. In this, lignosulfonates may be a minor but critically important component. This activity is justifiable if it requires special equipment and processing experience that cannot be readily duplicated by customers or competitors. For example, the use of lignosulfonate encapsulation techniques for the manufacture of controlled release nutrients, herbicides and insecticides in agriculture [57].

Experience in marketing, research, and development has shown several factors to be critical to success. The following appear applicable to lignosulfonates:

1. Organize for specialty operations, emphasize marketing and market development. Develop unique new processing and products. Cultivate alert, innovative and aggressive management practices.

2. Concentrate attention on a few carefully selected industries having growth

potential.   Seek out and satisfy emerging needs of industry in which the inherent properties of lignosulfonates are important.

3.   Offer different or better products to do a job.   Offer convenience, labor saving, improvement in customer operations, or reduced overall costs, not merely chemicals.

4.   Provide special products that the customer cannot easily make and which cannot be readily made by competitors.   Emphasize formulated chemical products, especially those requiring in-depth process know-how and specialized process equipment.

5.   Multiply the effectiveness of the sales force and reduce sales costs by working with specialty sales organizations that provide technical sales and detailed field service for functional chemicals sold.   Avoid commitments that arbitrarily restrict market coverage or limit sales.

6.   Know your own products and application technology.   Maintain customer loyalty by providing new products at reasonable intervals and by providing technical assistance.

7.   Conduct carefully directed pragmatic research and development aligned with objectives indicated by technological forcasting considerations.   Make full use of available technical information and license whenever appropriate.

It has been stated that the most common obstacles to a successful new product venture are impatience, insufficient planning and preparation, lack of undertanding of the market, and lack of necessary time, labor, and money to sustain the venture.

SUMMARY

Lignins and lignosulfonates have demonstrated their commercial value as chemical feedstock and their value in industry as functional chemicals.   Applied research has proposed commercial utilizations in thousands of patents and thousands of technical articles, the overwhelming majority of which remain dormant.

It is common for articles relating the chemical aspects of lignin usage to conclude with a statement to the effect that more research is needed with the implication that chemical research will someday surely provide the key to the volume use of lignin and lignosulfonates.

In recent years it has become fashionable to regard the probability of profitable volume use of lignin materials with pessimism.   For example, in the concluding remarks in the monograph "Lignins," the following statement occurs: "application research in the lignin field has not succeeded in bringing about glorious breakthroughs, and . . . such breakthroughs may not be anticipated in the future . . . ."

It is here contended that the "breakthrough" most required is not in research but in management.   Technical successes in applications research are not sufficient in themselves to achieve a breakthrough.   To achieve maximized value of spent sulfite liquor components, aggressive innovations in marketing, market development and management philosophies are required.

For the development of renewable resources, it may be well to emphasize profit and value instead of volume.

The basic question in "breakthrough" development concerns who is going to allocate the time, energy, and money to develop a solid major market based upon a

purchased raw material of dubious availability. With lignosulfonates in a low-profit disposable-waste status, a pulp mill will not hesitate to change furnish, cooking base, or pulping process if that is desirable from the standpoint of cellulose production or pollution control. Such changes, of course, may render the SSL lignosulfonate unavailable or unfit for an established use and leave a manufacturer without raw material.

In general, common prudence will negate construction of any multimegaton lignosulfonate processing facility that is dependent upon an outside uncontrolled raw material source. Only one such plant has been built, Milchem Nederland, which is a 1500 ton/month facility justified on the basis of a captive market [58].

It does appear that unless the forest products industry by itself, or in joint venture, assumes responsibility for process development, production and marketing of modified lignin derived products, it is quite possible that glorious breakthroughs will not occur.

It is possible that the wood chemicals industry will find justification to become more chemical process oriented because of the necessity for renewable resource development. Increasing emphasis may be placed upon fine chemicals and functional chemicals and less on pseudocommodities.

A forest products chemical-manufacturing entity utilizing captive raw materials, derived not only from lignin but also from wood sugars and cellulose, organized for the purpose of marketing fine chemicals and functional chemicals, might well be an economically attractive renewable resource diversification.

Consideration of past successful efforts in lignosulfonate utilization and current momentums in silvachemical product and market development gives promise that the wood chemicals industry can and will meet the lignosulfonate challenge.

REFERENCES

[1] H. J. Skinner, *Ind. Eng. Chem.*, *31*, 1331 (1939).
[2] Staff Report, *Chem. Eng. News, 41*, 83 (1963).
[3] Guy C. Howard, *Ind. Eng. Chem., 26*, 614 (1934).
[4] Guy C. Howard, *Ind. Eng. Chem., 22*, 1184 (1930).
[5] J. R. Salvesen and W. C. Browning, *Chem. Ind., 61*, 232 (1947).
[6] Marathon Corporation, *Marasperse Dispersants,* Bulletin M-553, (1947).
[7] Staff Report, *Modern Industry,* Aug. 15, 1952.
[8] J. H. Krieger, *Chem. Eng. News, 52,* 16 (1974).
[9] F. M. Ernsberger and W. G. France, *Ind. Eng. Chem., 37,* 598 (1945).
[10] J. Beekmans, *Can. J. Chem., 40,* 265 (1962).
[11] J. Le Bell, B. Bergroth, P. Stenius, and B. Stenlund, *Pap. Tra, 56,* 463 (1974).
[12] I. A. Pearl, *The Chemistry of Lignin,* Marcel Dekker, Inc., New York, 1967, p. 2.
[13] W. C. Browning, in F. Asinger (Ed.), *Chemistry, Physics and Application of Surface Active Substances,* Proc. IV Int. Congr. Surf. Act. Subs., Brussels, 7-12, Sept., 1964, Vol. I, Gordon and Breach Science Publishers, London, pp. 141-154.
[14] W. C. Browning, *J. Petrol. Technol., 7,* 9 (1955).
[15] J. R. Salvesen and W. C. Browning, U.S. Patent 2,533,632 (1950).
[16] W. C. Browning, U.S. Patent 3,047,494 (1962).
[17] Marathon Corporation, Chemical Div., Bulletin 110 (1949).
[18] Marathon Corporation, Chemical Div., Bulletin 109 (1949).
[19] H. R. Kruyt, *Colloids,* John Wiley & Sons, Inc., New York, 1930, pp. 67-80.
[20] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids,* Elsevier Publ. Co., Amsterdam, 1948.
[21] A. L. Johnson and F. H. Norton, *J. Amer. Ceram. Soc., 24,* 189 (1941).
[22] B. K. Asdell, *Paper Mill News,* May 31, 1947.

[23] E. W. Scripture, U.S. Patents 2,081,642 (1937), 2,127,451 (1938), 2,169,980 (1939), 2,229,311 (1941).
[24] J. G. Mark, U.S. Patent 2,141,570 (1938).
[25] W. C. Browning, *The Deflocculation of Clays in Solutions of Electrolytes,* paper presented at the Fifth National Clay Conference, Oct. 8–10, 1956, University of Illinois, Urbana, Illinois.
[26] P. A. Rehbinder, *Colloid J. USSR, 20,* 493 (1958).
[27] W. C. Browning, *Ind. Eng. Chem., 49,* 1401 (1957).
[28] M. van der Waarden, *J. Colloid Sci., 6,* 443 (1951).
[29] M. J. Vold, *J. Colloid Sci., 16,* 1 (1961).
[30] W. Heller, *Macromolecular Chemistry—2,* International Symposium on Macromolecular Chemistry, Prague, Czechoslovakia, 30 August–4 September 1965. Butterworths, London, 1966, pp. 249–274.
[31] W. C. Browning, *Can. Mining & Metallurgical Bull.,* November, 709 (1958).
[32] I. A. Pearl, *The Chemistry of Lignin,* Marcel Dekker Inc., New York, 1967, p. 297; Chap. 6
[33] C. H. Hoyt and D. W. Goheen, in K. V. Sarkanen and C. H. Ludwig, Eds., *Lignins,* Wiley-Interscience, New York, 1971, pp. 856–857; Chap. 13.
[34] W. C. Browning, A. C. Perricone, and K. Elting, U.S. Patent 3,677,961 (1972).
[35] W. C. Browning and B. G. Chesser, U.S. Patent 3.697,498 (1972).
[36] Von F. Patat, E. Killmann, and C. Schliebener, *Makromol. Chem., 49,* 200 (1961).
[37] H. E. Buckley, *Crystal Growth,* John Wiley & Sons, New York, 1961, Chap. 10.
[38] J. R. Salvesen, C. Harmon, and W. C. Browning, U.S. Patent 2,491,832 (1949).
[39] W. E. Barnes, U.S. Patent 2,491,436 (1949).
[40] W. C. Browning, U.S. Patent 2,800,449 (1957).
[41] W. C. Browning, U.S. Patent 2,771,421 (1956).
[42] W. C. Browning, *Trans. Soc. Petrol. Eng. AIME,* 231, (1964).
[43] Baddiley, Great Britain Patent 290,542 (1927).
[44] Philippi, Germany Patent 254,866 (1910).
[45] G. J. Byrd, U.S. Patent 2,858,271 (1958).
[46] E. G. King and Carl Adolphson, U.S. Patents 2,935,473 (1960), 2,935,504 (1960).
[47] A. Hayaski, Y. Namura and T. Uekita, *Mokuza, Gakkaishi, 13,* 194 (1967).
[48] A. Hayashi and N. Minari, *Mokuzai Gakkaishi, 13,* 198 (1967).
[49] W. C. Browning, Great Britain Patent 1,068,686 (1967).
[50] H. Tanaka and R. Senju, *Tappi, 53,* 1657 (1970).
[51] W. C. Browning and B. G. Chesser, U.S. Patent 3,669,042 (1972).
[52] W. C. Browning and B. G. Chesser, *J. Petrol. Technol., 24,* 1255 (1972).
[53] D. B. Uman, *New Product Programs,* American Management Association, Inc., 1969, Chap. 1.
[54] W. G. Kinsinger, "Chemical Marketing: The Challenges of the Seventies," *Advances in Chemistry Series, No. 83,* American Chemical Society, Washington, D.C., 1968, Chap. 12.
[55] *Chemical Marketing Reporter,* March 24, 1975, p. 7.
[56] C. H. Kline, *Organizing Specialty and Commodity Operations for Maximum Profit,* paper presented at European Chemical Marketing Research Association, Geneva, Switzerland, October 16, 1974.
[57] J. E. Flinn and H. Nack, *Chem. Eng., 74,* 171 (1967).
[58] *European Chemical News,* April 7, 1967, p. 25.

UTILIZATION OF HARDWOOD AS A CHEMICAL RAW MATERIAL IN LATVIAN SSR

A. Y. KALNINSH and N. A. VEDERNIKOV,

Institute of Wood Chemistry, Academy of Sciences of the Latvian SSR, Riga, U.S.S.R.

SYNOPSIS

A successful solution to the problem of complex utilization of hardwood is based on differential chemical action on the main wood components according to their properties, chemical structure and reactivity. It is possible to realize a directed conversion of pentosans to obtain furfural. At the same time the cellulose part of the raw material is preserved for subsequent processing. Yield of furfural reaches 70–80% of theory. Destruction of cellulose does not exceed 5–10%. Further chemical processing of the lignocellulose residue can be carried out by hydrolysis.

A new method for hydrolytic degradation of cellulose permits a shortening of the time required for the main hydrolysis from several hours to some minutes. The uniqueness of the method lies in conducting the process of cellulose destruction in solid phase in the presence of small amounts of concentrated sulfuric acid combining it with a simultaneous thermomechanic action on the hydrolyzed material. The sugar solution obtained can be used for isolation of crystalline glucose and formation of fodder yeasts.

INTRODUCTION

Wood is one of the main natural resources in the Soviet Union as well as in the Latvian SSR. This is why the problems of wood chemistry have been carefully studied by Latvian scientists for a long time. Recently, particular attention has been paid to utilization of hardwood as raw material for chemical processing. This process principally entails a complex chemical utilization of raw material and elaboration of new technological processes based on the results of theoretical investigations in the wood chemistry area.

RESULTS AND DISCUSSION

The most interesting chemical conversion of pentosans and polyuronides present in hardwood in an amount up to 30% is hydrolytic degradation to pentoses accompanied by subsequent dehydration of the pentoses to furfural.

125

The main principles of technological realization of the present process have been formulated in Ricard's patents [1]. Based on his recommendations all investigators proceeded from the assumption that hydrolysis of pentosans and dehydration of pentoses in a one-step furfural production from vegetable raw material is accelerated by a catalyst. According to this theory, uniform impregnation of the raw material with the catalyst solution is considered necessary. A reduction in the amount of this solution down to 30–40% against the weight of the raw material suggested by Miner and Brownlee [2] made the process of furfural production profitable and prompted industrial production but still has not been explained theoretically.

The results obtained at the Institute of Wood Chemistry in studies of submicroscopic wood structure, regularities in polysaccharides reactions with small amounts of strong sulfuric acid, and peculiarities in the diffusion of sulfuric acid and sugars in the cell wall, served as a basis for elaborating new theoretical principles for this technological process.

Production of furfural from wood and annual plants involves uniform impregnation of the material with dilute sulfuric acid subsequently treated with water vapors, the entire process proceeding in cell wall. Sulfuric acid penetrates into the cell wall, weakens the bonds hemicelluloses and cellulose and lignin, hydrolyzes hemicelluloses to monosaccharides and catalyzes the subsequent dehydration of the pentoses into furfural. In addition, deacetylation of hemicelluloses accompanied by acetic acid formation occurs when wood is treated with water vapors. However, as this acid is a weaker catalyst than sulfuric acid, it does not essentially affect the rate of hydrolysis.

Furfural molecules formed in the cell wall diffuse to the surface of the material enter the vapor phase and are removed from the reaction by a current of water vapor. Furfural formation from pentosans was shown to be kinetically controlled, provided the material is sufficiently subdivided. Although this process is complicated and involves many steps, it can be represented by the equation for the first-order monomolecular reaction [3]. Hydrolysis of pentosans proceeds 30–50 times faster in comparison to the following dehydration of pentoses into furfural under similar conditions [4]. This explains why the dehydration reactions alone, or rather one of them, determines the rate of the entire process of furfural formation and makes it conform to the requirements of a monomolecular reaction.

Difference in rates of both hydrolysis and dehydration leads to accumulation of substantial amounts of pentoses in the cell wall which react with intermediate dehydration products in the presence of sulfuric acid and at high temperature, resulting in formation of humic-like substances [5].

Furfural molecules formed in the cell wall react with intermediate products of pentose dehydration accompanied by formation of humic-like substances which diffuse to the surface of the material [6,7]. Besides, furfural (a compound of high reactivity), when affected by sulfuric acid, decomposes to formic acid and humic substances [8]. Furfural is oxidized forming peroxide compounds [9,10], and also reacts with lignin [11], tannins [12], and levulic acid [13]. All these secondary reductions of furfural proceed to a greater extent, the longer the time period from the point of its formation until the moment of its transfer to the vapor phase.

Accordingly, when vegetable materials are uniformly impregnated with dilute catalyst solution, all steps of the furfural formation process proceed directly in the cell wall. Furfural losses are substantial because of side reactions of pentoses and

secondary conversions of furfural. In this event furfural yield amounts to only 50-55% of theory.

In cooperation with Odintsov we have developed a hypothesis that hydrolysis of pentosans and dehydration of pentoses are accelerated differentially by acetic acid and sulfuric acid.

Due to the marked chemosorption heat, molecules of sulfuric acid absorbed on the surface of the particles are bound tightly to the polysaccharides by chemosorption bonds and do not penetrate into the particles. The strength of the chemosorption bonds between the sulfuric acid molecules and the polysaccharides increases with increase in initial acid concentration. It is slight for dilute solutions. As small amounts of sulfuric acid are used (3-6% of material weight), it covers only a small part of the entire surface of the particles.

Acetic acid, formed on treatment of wood with water vapors and distributed uniformly in the particles, catalyzes hydrolysis of hemicelluloses to monosugars. Further conversion of the pentoses to furfural directly in the cell walls does not take place because acetic acid is too weak a catalyst for dehydration at low temperatures. The pentoses formed diffuse to the surface of the particles where their dehydration to furfural occurs under the influence of the strong sulfuric acid.

The catalytic action on hydrolysis and dehydration is accordingly exerted differently by the acetic acid and the strong sulfuric acid. It makes it possible to lessen the difference in rates of these reactions. For instance, on using 10% sulfuric acid the rate of hydrolysis of pentosans exceeds by 30 times the rate of dehydration of the pentoses while with 90% sulfuric acid, the rate is only 6 times higher.
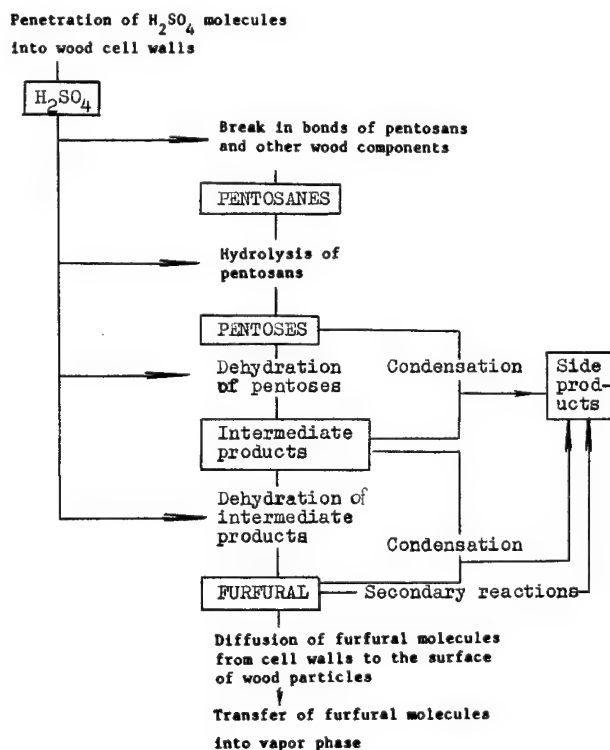
FIG. 1. Catalyst: 9% sulfuric acid in an amount of 30% based on dry wood.

Deacetylation of hemicelluloses by
treatment with water vapor

CH₂COOH

Break in bonds of pentosans and
other wood components

PENTOSANES

Hydrolysis of pentosans

PENTOSES

Diffusion of pentose molecules
from cell walls to the surface
of wood particles

Dehydration of pentoses

Intermediate products

Condensation

Side
products

Dehydration of intermediate
products

FURFURAL

Transfer of furfural molecules into
vapor phase

H₂SO₄
Adsorption and
hemisorption of
H₂SO₄ molecules
on surface of
wood particles

FIG. 2. Catalyst: 90% sulfuric acid in an amount of 3% based on dry wood.

Furfural formation on the surface of vegetable material particles enables it to vaporize rapidly, thus precluding the possibility of secondary reactions. Vart [14] indicated the absence of secondary furfural conversions in case of its formation on a division boundary. However, the methods proposed first by Vart and later by other investigators for obtaining furfural from pentoses could not be realized because of the complex and uneconomical equipment required.

A process carried out under low pressure enables a more rapid vaporization of the furfural, as its volatility increases as the pressure decreases. A reduction in pressure promotes a rapid removal of furfural from the reaction site because the amount of vapor being the same, its specific volume and linear rate in reaction region increase, resulting in an increase in yield of furfural [15]. Thus, the entire process from the time of mixing the vegetable material with the catalyst until the removal of the furfural formed from the reaction, can be represented by two schemes depending on the concentration of the applied catalyst (Figs. 1, 2).

It is quite evident that the second scheme is applicable only to the first process period. Concentration of sulfuric acid in the process gradually decreases, since the acid is diluted by moisture contained in the raw material, by vapor condensate formed on heating the material, and by water of dehydration. This results in a weakening of the bonds between the sulfuric acid molecules and the wood components. Sulfuric acid starts to diffuse into the particles. But acid diffusion is of a molecular character, while counterdiffusion of pentoses is of both molecular and

convection character, because the process is accomplished in a current of overheated vapor and is accompanied by water evaporation. Diffusion of pentose molecules to the surface of the particles therefore proceeds quicker than the counterdiffusion of sulfuric acid. This is why the differentiation between catalysis of hydrolysis and dehydration is preserved in the course of the process although its efficiency gradually decreases.

According to the second scheme, the process is unique in involving little cellulose destruction because the sulfuric acid is located on the surface of the material particles and does not penetrate into the cell walls. Accordingly, in the hydrolysis of pentosans according to the second scheme, furfural yield is 1.2–1.5 times greater than the yield of furfural obtained according to the first scheme, but the amount of cellulose destroyed is 3–5 times less. This is possible thanks to the markedly lower temperature of this process when strong sulfuric acid is used.

Based on the hypothesis of differentiated catalysis and further theoretical studies on the mechanism and kinetics of furfural formation, a new method for furfural production from hardwoods and other raw materials has been worked out at the Institute of Wood Chemistry, Latvian SSR [16]. This method has been successfully tested and industrially applied at two plants in producing furfural from oak wood with a 25% increase in yield in comparison with conventional methods using dilute sulfuric acid as a catalyst.

It is known that besides sulfuric acid, some mineral and organic acids and salt solutions can serve as catalysts for furfural production. In this connection the established relationship between chemical composition and physical and chemical properties of applied catalysts in the course of furfural formation from hardwood pentosans is of interest. For example, it was shown that in the case of using chlorides of some metals, the catalytic activity of cations depends on their polarization strength. It presents a nonlinear function of ionization potential of corresponding atoms [17]:

$$K = a_0 + a_1 J + a_2 J^2 + a_3 J^3$$

where K is the constant for rate of furfural formation, and J is the ionization potential of atoms in forming corresponding cations. Coefficients obtained in the present experiments under similar conditions were:

$$a_0 = -1.598 \times 10^{-3} \, \text{min}^{-1}$$

$$a_1 = +3.886 \times 10^{-4} \, \text{min}^{-1} \cdot \text{ev}^{-1}$$

$$a_2 = -1.662 \times 10^{-5} \, \text{min}^{-1} \cdot \text{ev}^{-2}$$

$$a_3 = +3.996 \times 10^{-7} \, \text{min}^{-1} \cdot \text{ev}^{-3}$$

Established relationships make it possible to progress from empirical selection of catalysts to scientifically valid selections and to elucidate the chemical mechanism involved.

Application of this new method for furfural production with its slight cellulose destruction which does not exceed 5–10%, permits a use of the lignocellulose residue for further chemical processing. It is more expedient to accomplish such processing by applying a new hydrolysis method [18,19], whose theoretical and technological principles have been elaborated at the Institute of Wood Chemistry, Latvian Academy of Sciences [20,21]. The new method of hydrolytic destruction of cellulose permits a shortening of the time required for the main hydrolysis from

several hours to some minutes. The key point of the method lies in conducting the process of cellulose destruction in the solid phase in the presence of small amounts of concentrated sulfuric acid, combining it with a simultaneous thermomechanic action on the hydrolyzed material. To realize this method, the problems of mixing raw material with small amounts of strong sulfuric acid [22], mechanical and chemical treatment of lignocellulose residue [23], inversion of the obtained hydrolyzate mass [24] and other problems have been solved.

At present this method is under pilot-plant testing. It makes it possible to obtain crystalline glucose, fodder yeasts and other valuable products besides furfural.

REFERENCES

[1] E. Ricard, French Patent 485967 (1917); German Patent 348147 (1917); U.S. Patent 1322054 (1919).

[2] C. S. Miner and H. J. Brownlee, British Patent 203691 (1923), 207116 (1923); French Patent 570531 (1923), 609191 (1925); German Patent 486293 (1923).

[3] A. A. Arsenyuk, *Tr. Voronezhsk. Khim.-Tekhnol. Inst., 7,* (1941).

[4] K. Schoenemann, *Chem. Eng. Sci., 8,* 171 (1958).

[5] A. Y. Kalninsh and V. K. Kalnina, *Izv. Akad. Nauk Latv. SSR, 11,* 87 (1949).

[6] A. Dunlop and F. Peters, *The Furans,* New York, 1953.

[7] D. F. Root, J. F. Saeman, and J. F. Harris, *Forest Prod. J., 9,* 158 (1959).

[8] N. I. Nikitin, *Wood and Cellulose Chemistry* (in Russian), Mowcow-Leningrad, 1962, p. 573.

[9] Y. I. Kholkin, *Zh. Prikl. Khim., 33,* 914 (1960).

[10] V. G. Kulnevich, K. M. Kardailova, S. V. Abramyants, and N. S. Maksimenko, *Izv. Vyssh. Uchebn. Zaved., Pishchev. Tekhnol., 2,* 93 (1966).

[11] A. P. Dunlop, *Ind. Eng. Chem., 40,* 204 (1948).

[12] A. P. Zakoshchikov, V. T. Ivanova, and Kurenkova, *Zh. Prikl. Khim., 5,* 235 (1932).

[13] H. Hosaka, *Rep. Hokkaido Forest Prod. Res. Inst., 15,* 32 (1959).

[14] C. Vart, V. Vaks, and C. Erben, German Patent 740602 (1943).

[15] N. A. Vedernikov and P. N. Odintsov, *Izv. Akad. Nauk Latv. SSR, Ser. Khim., 2,* 237 (1963).

[16] N. A. Vedernikov, P. N. Odintsov, A. Y. Kalninsh, and V. K. Kalnina, USSR Patent 151683 (1962); French Patent 1421046 (1965); Italian Patent 752841 (1967); Japan Patent 512090 (1968); Swedish Patent 322785 (1970).

[17] N. A. Vedernikov and A. Y. Kalninsh, *Wood Chemistry* (in Russian), Riga, 1972, Vol. 11, p. 111.

[18] P. Odintsov, V. K. Kalnina, and C. A. Sobolevskii, USSR Patent 105278 (1952).

[19] A. Y. Kalninsh, P. N. Odintsov, and I. I. Beinart, USSR Patent 106013 (1956).

[20] P. N. Odintsov, V. K. Kalnina, and N. A. Vedernikov, *Izv. Akad. Nauk Latv. SSR, Ser. Khim., 4,* 491 (1965).

[21] V. K. Kalnina, I. I. Beinart, and B. M. Taubin, *Riga Hydrolysis Method* (in Russian), Riga, 1961.

[22] N. A. Vedernikov, V. K. Kalnina, A. J. Rolle, U. K. Ziemelis, and G. K. Abolinsh, *Gidroliz. Proizvodstvo, 4,* 11 (1974).

[23] V. K. Kalnina, N. A. Vedernikov, and A. B. Veips, *Izv. Akad. Nauk Latv. SSR, Ser. Khim., 3,* 313 (1964).

[24] Z. O. Okonova, N. A. Vedernikov, and V. K. Kalnina, *Gidroliz. Proizvodstvo, 10,* 6 (1972).

ACID HYDROLYSIS AND DEHYDRATION REACTIONS FOR UTILIZING PLANT CARBOHYDRATES

JOHN F. HARRIS

Forest Products Laboratory,* Forest Service,
U.S. Department of Agriculture,
Madison, Wisconsin 53705

SYNOPSIS

The two major reactions of wood carbohydrates in aqueous acidic media are reviewed for their utilization potential. The extensive published information is reviewed, and its applicability to process problems is discussed. The available knowledge that may be used in resolving process problems includes: composition of polymers; mechanism and rate data for the hydrolysis of various glycosides, oligomers and polymers; as well as mechanisms and rate data for the degradation of monosaccharides and the formation of furans and other products. This suffices for making decisions on research and development projects. The author contends new work should be bench-scale rather than pilot-plant development. Much additional information is required before plant carbohydrates will be a major economic source for organic chemicals. The needed data can be obtained from small-scale studies that will extend the existing fundamental work. The general areas requiring research are stated here.

INTRODUCTION

Present and impending crises in the supply of nonrenewable resources have prompted evaluating extending these resources by using the renewable resources more efficiently. The huge quantities of available lignocarbohydrate residues—agricultural and logging residues, unused species, diseased trees, recycled material and underutilized process streams—are conceived as untapped wealth. It is inevitable that large sums will be spent to replace nonrenewable materials with renewable resources. Despite the great potential that has always existed in this area, research over the years has been sporadic and poorly financed. There is, however, a danger that money will be wastefully spent on inadequately designed development-type projects. Suitable utilization processes have not evolved to the development stage, and more work of a fundamental nature is needed.

This paper gives an overview of the knowledge available, relates it to the prob-
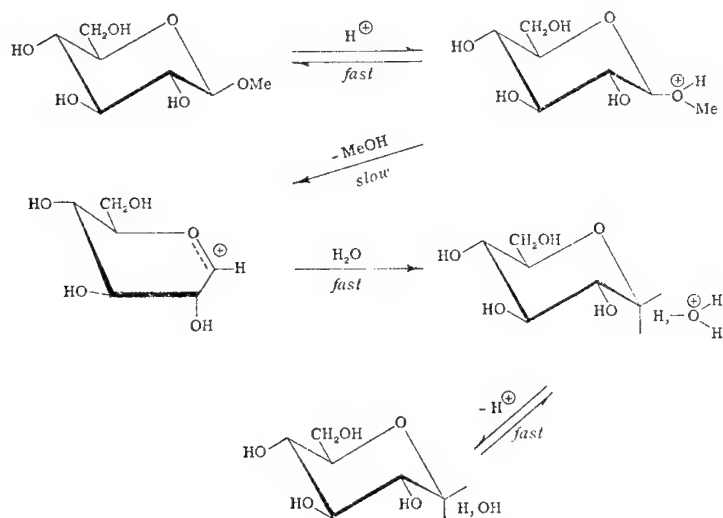
FIG. 1. Hydrolysis via the cyclic carbonium-oxonium ion.

lems of utilization, demonstrates its use in solving process problems, and indicates areas for further research. Lignocellulosics have been considered a source for energy, fodder, sugars, and chemicals. The problems in developing processes for each of these are different. The present discussion relates to only the sugars and chemicals; it will be arbitrarily restricted to acid treatment.

The choice of processing residues with acid or base reagents is rather a fundamental choice because of the great differences in process that result. The presence of acetyl groups and the degradation of labile hemicelluloses result in large amounts of organic salts in digesting liquors if basic reagents are used. This presents entirely different recovery problems than does the presence of the free acids and carbohydrates in acidic digestion liquors.

If polymeric carbohydrates are treated with an aqueous acidic reagent, two types of reactions of overriding importance occur: glycoside hydrolysis and dehydration. These have been intensively studied for many years; acidic cleavage of the glycosidic bond has been studied for more than a century. The hydrolysis mechanism and the reaction rates of simple glycosides, disaccharides, and oligosaccharides and polysaccharides also have been investigated. Much of the confusion in interpreting results has been resolved with the concepts of conformational analysis. Some aspects remain unclear, but it can be said that the general principles are well understood. The subject of glycosidic bond cleavage has been frequently reviewed in articles on homogeneous [1–4] and heterogeneous reactions [5,6].

HYDROLYSIS

Excepting those pyranosides that contain a stable ion aglycon, fragmentation occurs through fission of the glycosyl-oxygen bond. This has been shown true for methyl and phenyl α- and β-D-pyranosides, maltose, and methyl 2-deoxy-α-D-glucopyranoside [7,8], and reasonably assumed true for glycosidically linked polysac-
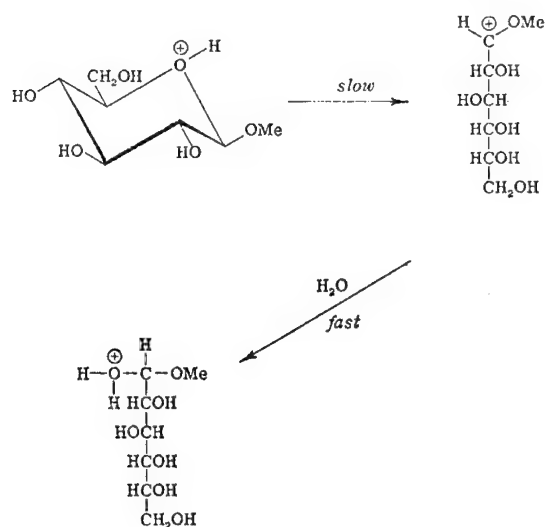
FIG. 2. Hydrolysis via the acyclic carbonium ion.

saccharides. The logarithm of the hydrolysis rate of any particular glycoside varies linearly with the Hammett acidity function. It is generally agreed that the reaction proceeds through initial protonation of one of the hemiacetal-oxygen atoms to form a conjugate acid. Depending on the particular atom protonated, one of two mechanisms is possible. Protonation of the glycosidic oxygen (Fig. 1) leads to elimination of the aglycon by fission of the C-1 to exocyclic 0 bond and formation of a cyclic carbonium ion. Protonation of the ring oxygen (Fig. 2) results in ring opening and formation of an acyclic ion. The resulting hemiacetal would hydrolyze rapidly to the free sugar.

Much debate has centered on which mechanism is operative or if both mechanisms are operative. The case for the cyclic carbonium ion intermediate is considerably strengthened by the work of Capon [9] who found methyl D-glucosides are anomerized in fully deuterated methanolic methanesulfonic acid with virtually complete exchange with the solvent. Proponents for either mechanism visualize the site of protonation exclusively at one or the other of the hemiacetal oxygens.
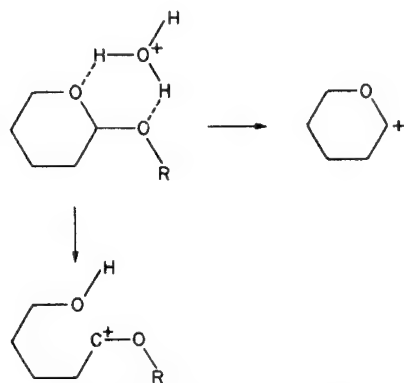
FIG. 3. Distributed protonation.
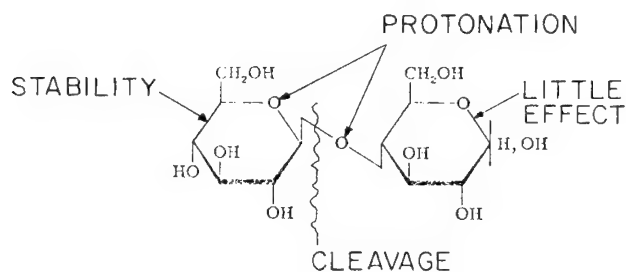
FIG. 4. Factors in glycoside hydrolysis.

Apparently, because of the structured nature of water, both oxygens will be partially protonated as shown in Figure 3. Thus, the conjugate acid of both mechanisms will be the same, and the position of cleavage will depend on the electron-density distribution in this six-membered ring. Accepting this structure will change the interpretation of electronic effects, C-2 influence, and isotope-rate effects.

The principles of conformational analysis have probably been the most revealing factor in interpreting glycoside hydrolysis rates. It has been convincingly demonstrated that the rotational energy barrier encountered in ring flexure is a fundamental rate-controlling factor; i.e., the rigidity of the glycon ring controls the hydrolysis rate. This simple concept puts order into a large amount of data; the pyranosides of pentoses and hexoses fall regularly into place, substitution on the ring results in a decreased hydrolysis rate, and furanosides react much faster than do pyranosides.

These ideas may be applied unequivocally to interpret the hydrolysis rate data of β-(1–4) linked oligosaccharides. Table I shows the rates in dilute acid for β-methyl pyranosides and β-(1–4) disaccharides fall in the same order determined by the ring stability of the glycon. The effect of the aglycone, although sizable, is not as great as the ring-stabilizing effect. The basic principles of glycoside hydrolysis are summarized in Figure 4.

The glycosidic bonds in cellotriose, Figure 5, have different stabilities because

TABLE I

Relative Hydrolysis Rates of Methyl-β Pyranosides and (1–4)-β Linked Disaccharides

Methyl pyranoside of:		Disaccharide	
β-D-Glucose	1.0	Cellobiose	1.5
		Glucosyl–Mannose	1.5
		Pseudocellobiouronic acid	1.5
β-D-Mannose	3.0	Mannobiose	2.7
β-D-Galactose	4.8	Lactose	3.6
β-D-Xylose	5.8	Xylobiose	11.0
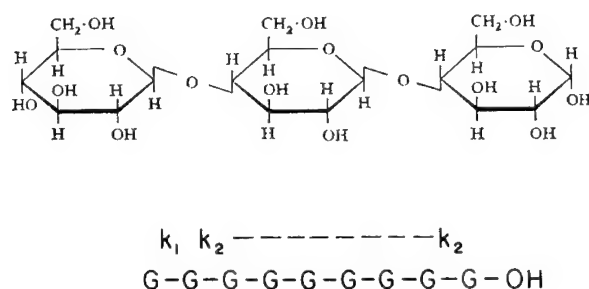
FIG. 5. Cellotriose and an anhydroglucose oligomer.

they have different glycons. The rate of hydrolysis of the glycosidic bond at the nonreducing portion of the molecule is 50% higher than that of the bond at the reducing portion, and the stability of the bond at the nonreducing end is approximately the same as that of cellobiose [10]. If it is assumed that a further increase of the chain length has only a minor effect on the cleavage rate, a simple kinetic model for the hydrolysis of oligoglucans can be formed. The terminal glycosidic bond at the nonreducing end is assumed to hydrolyze at one rate, whereas all others hydrolyze at the same but somewhat lower rate. Thus the two kinetic constants that describe the hydrolysis of cellotriose completely describe the homogeneous hydrolysis of cellulose.

The model was proposed in 1930 by Freudenberg et al. [11] who with Blomquist [12] in 1935 measured the rate of hydrolysis of solubilized cellulose, cellotetraose, cellotriose, and cellobiose in 51% sulfuric acid. Measurements on the series were extended to cellopentose and cellohexaose by Wolfrom and Dacons [13]. Although it was not possible for these investigators to obtain the individual bond cleavage rates, their data for total hydrolysis rate may be satisfactorily correlated with Freudenberg's model, assuming a rate between 2.5 and 3.0. This is considerably greater than the value of 1.5 measured using radioactive cellotriose [10].
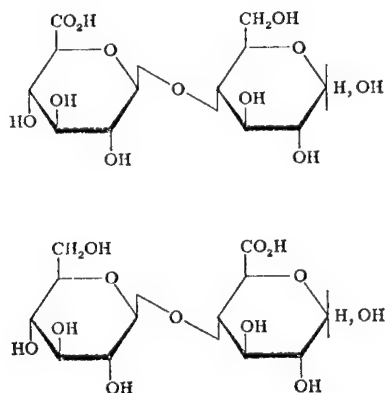
FIG. 6. Cellobiouronic and pseudobiouronic acids.

$$\beta\text{-}\textrm{D-Xyl}p\text{-}(1 \rightarrow 4)\text{-}\beta\text{-}\textrm{D-Xyl}p \qquad \beta\text{-}\textrm{D-Xyl}p\text{-}(1 \rightarrow 4)\text{-}\beta\text{-}\textrm{D-Xyl}p$$

```
      β-D-Xylp-(1 → 4)-β-D-Xylp        β-D-Xylp-(1 → 4)-β-D-Xylp
              2                                        2
              ↑                                        ↑
              1                                        1
      4-O-Me-α-D-GpA                          4-O-Me-α-D-GpA


           1                                    2
```
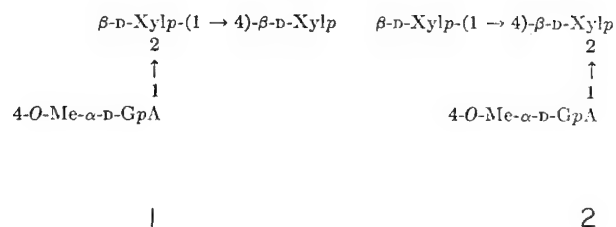
FIG. 7. Aldotriouronic acid isomers.

However, the presence of reversion products in the strong acid medium may have introduced serious errors in the work of these investigators.

The structures of the major hemicelluloses were known in reasonably good detail by the mid-1960s. The history of this development and a detailed discussion of the state of the knowledge at that time are given in an excellent review by Timell [14,15]. Examination of these structures shows that, with the exception of arabinogalactans that are β-(1–3) linked, the backbones of these polymers are joined β-(1–4). They are substituted (branched) at various points with carbohydrates of one to five units in length, most frequently a monosaccharide. The attachment at these branch points is invariably glycosidic. Thus it would seem that under acidic hydrolysis conditions, the side chains would be rapidly removed, leaving residual linear fragments of the β-(1–4) linked backbone. This is, in general, true with the one important exception occurring when the substituent is 4-0-methyl-D-glucuronic acid that occurs in hardwood xylans.

Glucuronosides are much more resistant to hydrolysis than are glucosides. Johansson et al. [16] found that cellobiouronic acid (Fig. 6) hydrolyzed at less than a thirtieth of the rate of pseudo-cellobiouronic acid which, as noted, hydrolyzes at the same rate as cellobiose. The ratio reported for other glucoside/glucuronoside pairs is not as great, ranging from 2.3 to 19. The 2-**0**-(4-**0**-methyl-α-D-glucopyronosyl)-D-xylitol/2-**0**-(4-**0**-methyl-α-D-glucopyronosyluronic acid)-D-xylose ratio has been reported as 18 [17]. The explanation of the manner in which the carboxyl group at C-5 affects the hydrolysis rate is as yet unknown.

In applying this information to the hydrolysis of hemicellulose, the general principles taken from the work on pyranosides and disaccharides are found of value. β-(1–4) linked polymers of glucose, xylose, mannose, and galactose hydrolyze in homogeneous solution in the ratios 1:3.5–4:2–2.5:4–5 [3]. Excepting the case in which 4-O-methyl-gluronic acid is the substituent, all of the short side groups are labile; the heterogeneous backbone of the galactoglucomannan, prevalent in softwoods, disintegrates to the expected ratios of various disaccharides and trisaccharides. An interesting calculation of Lindberg's is discussed in Timell's review [14,15]. Hardwood xylans degrade readily, and the presence of sizable amounts of aldotriouronic acid of type 1 and absence of type 2 attests to the validity of these general principles (Fig. 7).

The heterogeneous hydrolysis rate of cellulose is 1–2 orders of magnitude less than that of glycosides and will appear, at first, a rather different phenomenon. The major added factor to consider is the morphology of cellulose; here, despite the large effort on this problem, our ignorance is great. Apparently, even the parallel or antiparallel aspect has not yet been resolved [18].

A typical weight loss versus time curve for the dilute hydrolysis of cotton cellu-
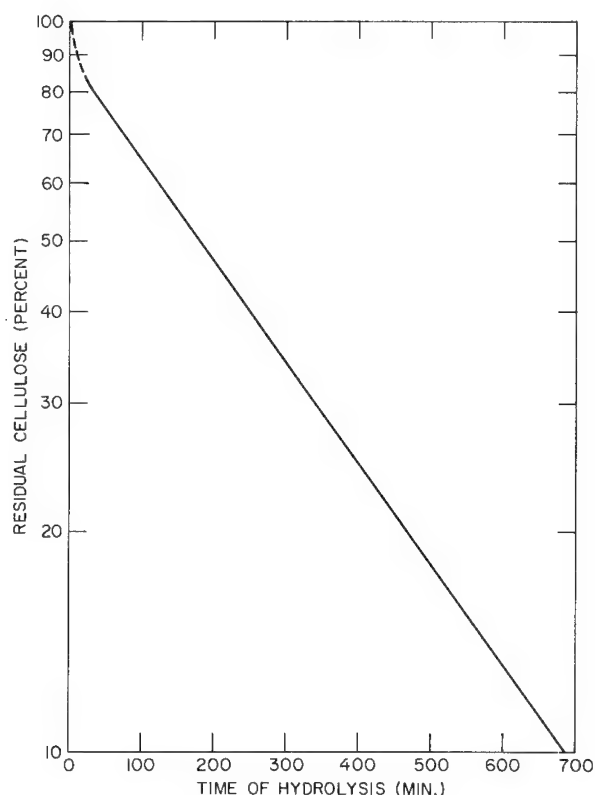
FIG. 8. Cellulose weight-loss vs. time curves for acid hydrolysis (constant boiling HCl, 760 mm).

lose is shown in Figure 8. It has two notable features: the rapid removal of a significant amount of material and the subsequent slow, linear (on the semilogarithmic plot) portion of the curve that extends to almost complete solution (97%). The degree of polymerization of the residual solid (not shown) follows a similar pattern with a large initial drop in the early stages of hydrolysis followed by a slow decrease. These facts are most familiar. They have become entrenched in the literature: "amorphous fraction," "limiting DP" and "first-order reaction."

The linear portion of the weight-loss curve extends from about 90% to as low as 3% residue. The material undergoing hydrolysis throughout this stage is composed of crystallites extremely resistant to hydrolysis. No kinetic model has yet been proposed that fits the experimental data. If it is assumed that all glycosidic bonds cleave at random, following first-order kinetics, the weight-loss curve departs rapidly from linearity. Attempts have been made to model the system by supposing that only the crystallite surface is available for reaction. These correlations fit the data less adequately than does the simple first-order kinetic model. The correlations serve only to disprove the hypothesis. Considering the structure of the cellulose crystallite and its hydrophilic nature, it is probable that hydrated protons could move freely throughout the lattice. It is even perhaps not necessary that proton movement accompany bond cleavage. Because of our knowledge of glycoside hydrolysis, the most tenable hypothesis would be to ascribe the hydrolysis resistance to the rigidity of the rings held tightly in the crystal structure.
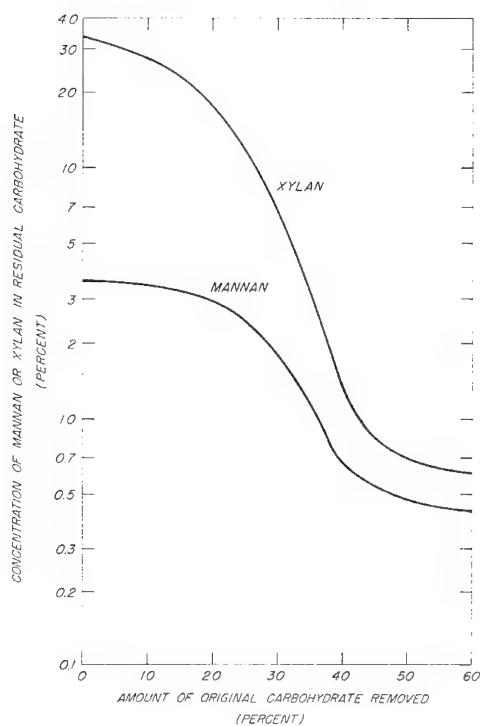
FIG. 9. Variation of residual carbohydrate composition during hydrolysis of red oak.

Explanation of the rapid initial rate of dissolution of cellulose is also possible on the basis of the knowledge of simple models. If it is assumed that the cellulose molecule has a folded structure, an assumption that is becoming more in vogue is that the folds may simply consist of a different conformer of the pyranose ring, that is, something other than the C1 conform. Such high-energy groups located
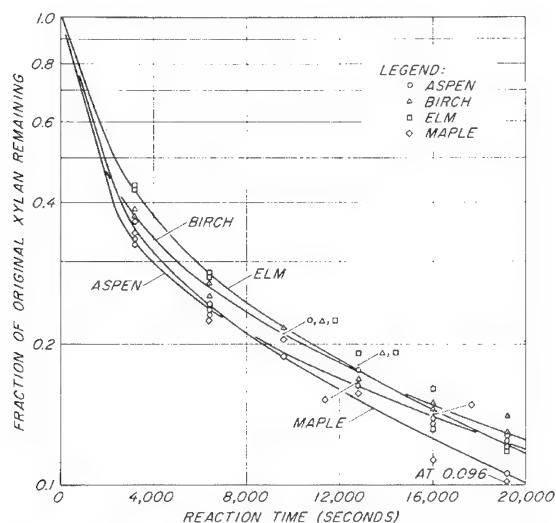
FIG. 10. Xylan weight-loss vs. time curves for acid hydrolysis (0.1N HCl, 120°C).

at the extremities of the crystallite would be expected to be readily hydrolyzable.

Despite the great complexity of lignified plants, both in physical and chemical nature, the information given here can be successfully used to interpret and estimate process data. The complexities include the presence of lignin, its distribution throughout the cell, the unknown nature and extent of bonding of lignin with the carbohydrates, and the nonhomogeneous distribution of the various polysaccharides and their close association with one another.

Under dilute acid hydrolysis conditions, the major carbohydrate components have been found to hydrolyze at about the same relative rates regardless of the particular reaction conditions. This is illustrated in Figure 9 that relates the mannan (mannose) and xylan (xylose) content of the residue to the residual carbohydrate yield [19]. This species-dependent relationship is found to hold for a rather wide range of processing conditions and also to be independent of the presence of a lignin solvent. Obviously, this type of relationship is only an approximation to the fact, but it is a generalization of interest from a process viewpoint. In conjunction with kinetic data on the system, it can be used to predict yields and compositions of the various products as conditions of processing are changed.

The difference in removal rates between hemicelluloses is large, but the rates fall into an expected pattern. For a particular set of hydrolysis conditions, there is an initial period of rapid removal followed by a much decreased rate as shown in Figure 10 [20]. The mannans of softwoods are more resistant than the hardwood xylans, and among the hardwoods, those containing xylans with high uronic acid contents lose their xylan less readily. The presence of a delignifying reagent, such as a hydrotropic salt, increases the rate appreciably.

The point at which the removal rate decreases and the subsequent magnitude of the rate are apparently functions of cell structure and the distribution of components. Complete removal of the hemicelluloses is not obtainable, but to reach the levels shown (>90%) requires rather high acidities or simultaneous lignin removal. In considering wood as a potential organic raw material, this is an important research area. Because of our present knowledge and improved techniques, some significant work could be done that would lead eventually to the development of a commercially viable process for solubilizing hemicelluloses and lignin to leave a relatively pure glucan.

SUGAR DECOMPOSITION AND SACCHARIFICATION

The major reactions associated with the production of sugars from wood are the hydrolysis of the polymer and destruction of the resulting monosaccharides. Considerable information is available on the rates of sugar decomposition in dilute acid solutions; very little, in strong acid media. Greatest stability is in the pH range 4–6. The order of stability in dilute acid (to 2N) differs from the order of glucoside stability being xylose < arabinose < mannose < (glucose ≈ galactose). Galactose and glucose are of approximately equal stabilities, their order changing with acid concentration and temperature. Smuk and Zoch of this Laboratory have found this order to correlate with the nonbonded energy differences of the stable conformations of pyranose rings.

With the hydrolysis and decomposition rates available, calculations of yield can be undertaken. From the hydrolysis of hardwoods, good yields (70–80%) of xy-
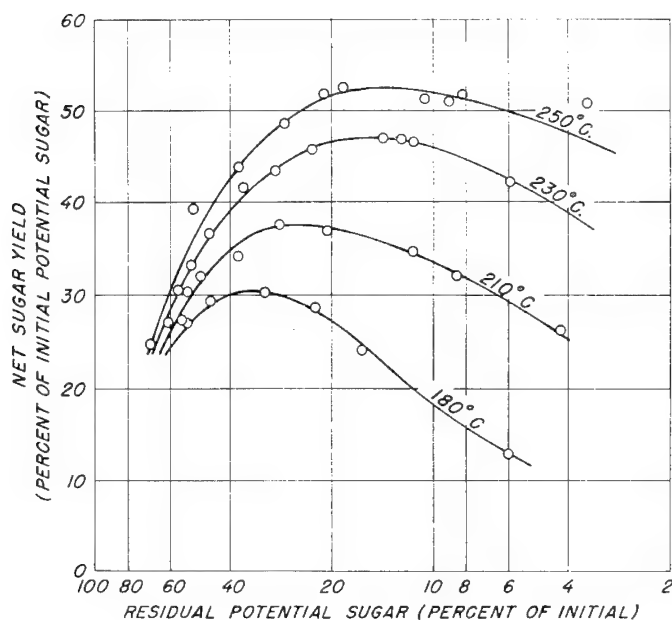
FIG. 11. Net sugar yields from cellulose, 0.4% H_2SO_4.

lose can be obtained despite its instability. This results from the relative ease of hydrolysis of the hemicellulose fraction. This does not result in the hydrolysis of cellulose that is unique among the polysaccharides in its resistance to hydrolysis.

Although the reaction mechanism for the heterogeneous hydrolysis of cellulose is undoubtedly complex, the experimental data for glucose yield can be well represented by the simple equation describing first-order consecutive reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
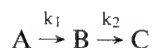
where k_1 and k_2 are first-order rate constants.

The maximum concentration of component B is a function only of the ratio of the rate constants, independent of their absolute value. Saeman [21] found this ratio favorably affected by increasing either the temperature or the catalyst concentration. The marked increase in yield resulting from increased temperature is shown in Figure 11. These yield increases have a great impact on process economics. They mean not only lower plant and raw material costs, more concentrated solutions, but possibly of greatest importance, higher quality solutions. If
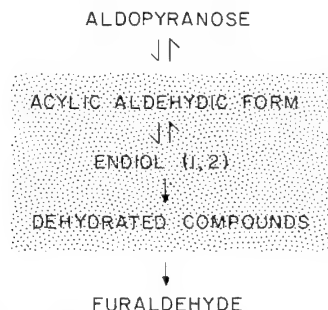
FIG. 12. Mechanism of sugar dehydration.

yield is increased from 30% to 50%, the impurity to sugar ratio drops from 2.3 to 1.0. The problem of putting these results into practice is, of course, the high pressures involved (>300 lb/in.^{2}); this is one area in which research development funds might be profitably spent.

Other suggestions have been made for favorably increasing this kinetic ratio such as β-ray irradiation, preheating, and fine grinding, but none has yet shown commercial promise. The use of enzymes to hydrolyze cellulose circumvents the problem of sugar destruction; thus raises yields dramatically. Unfortunately, the rate of attack on lignified crystalline cellulose is so slow that an inexpensive pretreatment of some sort seems a necessary part of the process to make it practical.

Many cellulose solvents are prominent; among them are the strong mineral acids. Several saccharification processes have been based on their use. The major economic problem is recovering the large amount of expensive reagent required.

In a scheme of complete utilization of the wood carbohydrates, in which the lignin and the hemicelluloses are first removed, leaving a glucan of relatively high purity, cellulose solvents apparently have a role. Considered as a means of producing glucose it is necessary to develop methods of recovering the expensive solvent, i.e., separating the oligosaccharides and monosaccharides from the dissolving reagent. Perhaps more promising is the possibility of reacting the dissolved sugars, *in situ,* to produce chemicals more easily recoverable and of higher value than the sugars. Considered in this manner, it may be economical to use rather expensive cellulose solvents. The study of glucose reactions in various cellulose solvents is a promising and interesting area of research.

DEHYDRATION

The reaction of carbohydrates in acidic solution results in a myriad of products. With the exception of anhydrosugars and oligosaccharides found as concentration-dependent equilibrium constituents, all of the products result from reactions of intermediates in the Lobry de Bruyn-Alberda van Ekenstein transformation. The main course of the reaction of aldoses is shown in Figure 12. The compounds included in the shaded area are highly reactive, occur in very low concentration, and are not readily isolated. Proof of their existence and function in the reaction is based primarily on indirect evidence [22]. It can be inferred that the stability of the ring structure is an important factor in determining the overall rate constant, that those sugars with an unstable ring structure will degrade most rapidly. This is true, but other factors of lesser importance also are involved.

The production of furfural from xylose has been studied intensely [23]. Since furfural is unstable under dehydration conditions, its concentration in the reacting medium follows a typical growth-and-decay curve. Independent measurements of the decomposition rates of xylose and furfural may be made, and the kinetic constants used to correlate the appearance of furfural in the homogeneous reacting medium. It develops that, unlike the cellulose-glucose system, the mechanism is not a simple pair of consecutive first-order reactions. Furfural reacting alone does not disappear by a first-order mechanism; its velocity constant is dependent on the initial concentration. Also, there is a very large yield-reducing interaction between intermediates formed from xylose and furfural. Nevertheless, an empirical
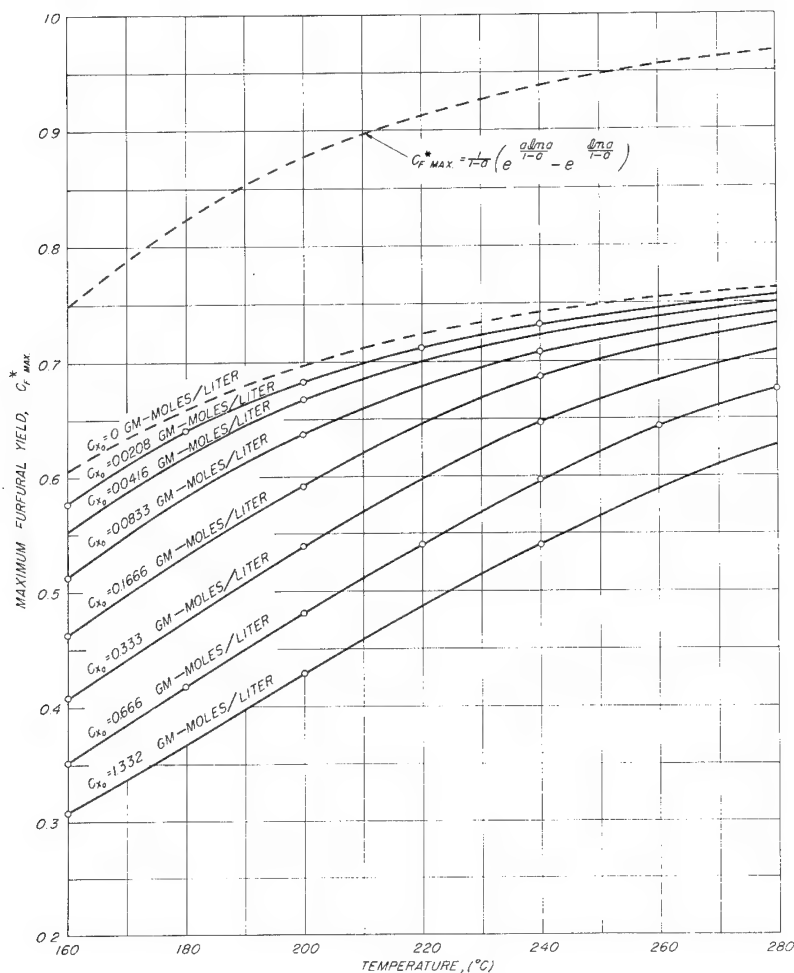
FIG. 13. Maximum furfural yields for acid concentrations greater than 0.1N H_2SO_4.

correlation, suitable for use under nonisothermal conditions, has been developed. Maximum furfural yields from xylose solutions are shown in Figure 13. Notice the large difference of the actual yield from that predicted for a mechanism of consecutive first-order reactions and the favorable effect of increasing temperature or decreasing sugar concentration. These data, obtained using pure xylose solutions, were found applicable to wood hydrolyzates [24] if allowance was made for the buffering effects of the salts present.

From the chemical knowledge available, the yields of hydroxymethylfurfural (HMF) from glucose would be expected to be significantly lower than those of furfural from xylose. This results from two factors: the greater stability of the glucopyranose ring and the greater instability of the furan. HMF disappears by an entirely different mechanism than does furfural, a result of the presence of the hydroxymethyl substituent. The mechanism is shown in Figure 14. The insolable, relatively stable end product of the sequence is levulinic acid formed in high yield (approximately 85%). The reaction is first-order, and occurs at a rate tenfold greater than the disappearance of furfural. In dilute mineral acid solutions the yields of HMF from glucose are low (10–20%), whereas the yields of levulinic acid
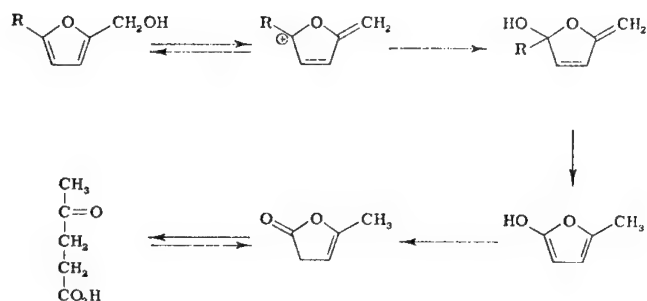
FIG. 14. Mechanism of levulinic acid formation.

range from 30–50%. At low catalyst concentrations the HMF yields are only slightly affected by increasing acid concentration, but examination of some of the analytical procedures will indicate that very high yields are obtained in strong sulfuric acid. This may result from the low availability of hydroxyl ions in this medium.

Increased yields of furans from monosaccharides can be obtained by decreasing the ring stability, shifting the equilibrium to the acyclic forms, increasing the stability of the product, and by decreasing the interaction of intermediates. Some possibilities are obvious, such as the isomerization of glucose to fructose, but the system is too complex to make predictions about the effect of catalysts and additives or variation in processing conditions. We have found that some simple aqueous inorganic catalyst systems can increase yields of HMF from glucose into the 35–45% range. The presence of secondary amines also apparently has a beneficial effect.

The present discussion has demonstrated that a significant amount of information is available for preliminary estimation of the commercial feasibility of processes based on acid hydrolysis. Estimates may be made of yields, rates, and solution and residual composition. All research and development projects should be preceded by these calculations. Currently, only the development of a high-pressure saccharification process is apparently suitable for implementing in research and development; however, other processes may be feasible. Present research should be at the bench-scale level. The extensive scientific information available permits the skillful design of experiments to gather data on process significance, but needs not be predicted on the success of a new process. Properly designed experiments can yield data applicable to existing industries while being part of a program for utilization of renewable resources.

REFERENCES

[1] B. Capon, *Chem. Rev., 69,* 407 (1969).
[2] F. Schafizadeh, *Advan. Carbohyd. Chem., 13,* 9 (1958).
[3] J. N. BeMiller, *Advan. Carbohyd. Chem., 22,* 25 (1967).
[4] C. A. Vernon, *Proc. Roy. Soc. B, 167,* 389 (1967).
[5] J. N. BeMiller, in R. L. Whistler and E. F. Paschall (Eds.), *Starch Chemistry and Technology,* Academic Press, New York, 1965, *1,* Chapter XX.
[6] A. Sharples, in N. M. Bikales and L. Segal, (Eds.), *Cellulose and Cellulose Derivatives,* Part IV, Wiley-Interscience, New York, 1971, V, Chapter XVIII.
[7] C. A. Bunton, T. A. Lewis, D. R. Llewellyn, and C. A. Vernon, *J. Chem. Soc.,* 4419 (1955).

[8] C. Armour, C. A. Bunton, S. Patai, L. H. Selman, and C. A. Vernon, *J. Chem. Soc.*, 412 (1961).

[9] B. Capon, *Chem. Commun.*, 21 (1967).

[10] M. S. Feather and J. F. Harris, *J. Amer. Chem. Soc., 89*, 5661 (1967).

[11] K. Freudenberg, W. Kuhn, W. Durr, F. Bolz, and G. Steinbrunn, *Ber., 63*, 1510 (1930).

[12] K. Freudenberg and G. Blomquist, *Ber., 68*, 2070 (1935).

[13] M. L. Wolfrom and J. C. Dacons, *J. Amer. Chem. Soc., 74*, 5331 (1952).

[14] T. E. Timell, *Advan. Carbohyd. Chem., 19*, 247 (1964).

[15] T. E. Timell, *Advan. Carbohyd. Chem., 20*, 409 (1965).

[16] I. Johansson, B. Lindberg, and O. Theander, *Acta Chem. Scand., 17*, 2019 (1963).

[17] R. L. Whistler and G. N. Richards, *J. Amer. Chem. Soc., 80*, 4888 (1959).

[18] M. M. Y. Chang, *J. Polym. Sci., 12*, 1349 (1974).

[19] J. F. Harris, J. F. Saeman, and E. G. Locke, in B. L. Browning, (Ed.), *The Chemistry of Wood*, Interscience, New York, 1963, Chapter 11.

[20] E. L. Springer and L. L. Zoch, *Tappi, 51*, 214 (1968).

[21] J. F. Saeman, *Ind. Eng. Chem., 37*, 43 (1945).

[22] M. S. Feather and J. F. Harris, *Advan. Carbohyd. Chem. Biochem., 28*, 161 (1973).

[23] D. F. Root, J. F. Harris, J. F. Saeman, and W. K. Neill, *Forest Prod. J., 9*, 158 (1959).

[24] J. F. Harris and J. M. Smuk, *Forest Prod. J., 11*, 303 (1961).

RECOVERY OF PENTOSES AND HEXOSES FROM WOOD AND OTHER MATERIAL CONTAINING HEMICELLULOSE, AND FURTHER PROCESSING OF C5- AND C6-COMPONENTS

HARALD F. FUNK

Silvichem Corporation Limited,
A-5084 Grossgmain-44, Salzburg, Austria

SYNOPSIS

The Silvichem process was devised to allow the recovery of hemicelluloses, i.e., pentoses and hexoses, without any damage of the fiber (cellulose) and without loss of lignin. The extract from this hydrolysis, largely xylose and glucose, can be processed further to separate C_5 and C_6 components. Xylose, for instance, can be processed to turn out derivatives such as xylitol (a sweetener, humectant, plasticizer and surfactant), xylonic acid (adhesive), trioxyglutaric acid (sequestering agent), or xylose-stearate (emulsifier). Furthermore, through polymerization and fermentation, a variety of other products can be obtained, such as polyols, polysaccharide gums, proteins, vitamins, and others. With the availability of xylose, a new line of chemistry can accordingly be established.

INTRODUCTION

Undoubtedly, the most vital and ingenious process is photosynthesis, which uses the most abundant raw material, i.e., water and a waste product (CO_2), and with the aid of the sun's energy, plus a catalyst, the building block of nature is formed plus oxygen. The chemical formula of this process is very simple:

$$nH_2O + nCO_2 = C_nH_{2n}O_n + nO_2$$
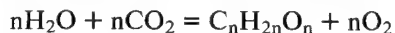
Biochemists were eager to simulate this synthesis but so far have been unable to realize it commercially.

In this connection, it is interesting to hear what an architect has to say, so that this issue can be seen from another angle:

"We build our big, black, glass-covered panels half a house long, and store the collected energy in expensive heat tanks or electric batteries, and throw in backup systems using conventional heaters. Yet, all around us the earth's oldest and most proven solar collector—leaves (which are green and never black, by the way)—turn solar energy directly into the sugars and other nutrients we can

145

TABLE I
Composition of Wood

Component	Softwood[a] (Spruce) %		Hardwood[b] (Beech) %
Cellulose		41.0	42.3
Hemicelluloses Hexosan Pentosan	19.0 5.8 }	24.8	5.6 23.7 } 29.3
Acetyl		1.4	3.9
Lignin		28.0	20.8
Others		4.8	3.5
		100.0	99.8

[a] Hägglund, Svenskkem, Tids Kr. 123 (1933).
[b] Runkel & Lange, Zellulose Chemie 185 (1931).

store and eat whenever the need for additional body heating or cooling is felt."

Mr. Malcolm Wells, renowned in his field, is referring to photosynthesis, the most vital process that supplies all life forms with energy as well as building blocks for natural materials. While man cannot oompete with nature, the available natural products and their basic building blocks (pentoses and hexoses) should be used more efficiently. The experts in the field of energy production and conservation are also concerned with this issue since only a small portion (less than 0.1%) of the 173 trillion kilowatts of solar energy transmitted to earth daily is fixed in living plant tissue. This "biomass," comprising all matter which grows, ought to be used effectively.

The record of the forest products industry in utilizing its main raw material, wood, is far from perfect. The lumber and pulp and paper industries are wasting about 50% of their raw material in their operations. On top of that, statistics show that 10 times more wood is destroyed by forest fires than is being utilized. While the wastage continues, today there are fuel, food and raw material shortages. Therefore, it is imperative to utilize natural resources to full advantage. This can be done only if wasteful industrial processes and technologies are changed.

WOOD SACCHARIFICATION

An alternative to wasting over half of the tree is the consideration of wood as a chemical raw material. More specifically, it should be possible to recover the hemicellulosic pentoses and hexoses from wood and still utilize the fiber for other products. Table I shows that softwoods and hardwoods contain about 25% to 30% of hemicelluloses.

While wood is known to be the oldest building material, the art of papermaking from wood is relatively young. It was 1844 when Keller in Germany invented a mechanical pulping process, and only 10 years later a patent on wood saccharification was granted to G. F. Melsens in Paris. Since then, numerous attempts have been made to produce sugars from wood, but only a few processes were exploited commercially.

In essence, there are two approaches to wood hydrolysis: (a) use highly concentrated mineral acids at ambient or low temperatures, or (b) use diluted acid concentration applied at high temperatures (up to 200°C) and corresponding high pressures. For instance, Bergius has used highly concentrated hydrochloric acid (up to 41%) at ambient temperatures. This process was modified later and is known as Rheinau-Udic process. The process developed by Scholler (known as the Scholler-Tornesch process) used 0.5% H_2SO_4 in up to 12 cycles where the temperatures are increased up to 180°C. Both these processes yield up to 80% of the recoverable sugars.

Variations of the Scholler process have been applied in the U.S.A. where the Madison process (developed by the Forest Products Laboratory in Madison, Wisconsin) has produced similar results but with lower utility consumption of 2.25 tons of steam as opposed to 6.25 tons used in the Scholler process.

The process developed in Peoria, Illinois, by Northern Regional Research Laboratory, as well as Giordani in Italy, uses concentrated sulfuric acid. On the other hand, the Hokkaido process is based on treatment with a low concentration of H_2SO_4 in the prehydrolysis phase then yielding furfural, while in the main hydrolysis phase an 80% concentration of sulfuric acid at room temperature is used. Posthydrolysis again is carried out with a low concentration of the same acid which is recovered. Crystalline glucose is produced through a glucose–sodium chloride double salt.

The Nippon-Mokuzai-Kagaku process is geared for the production of crystalline xylose besides crystalline glucose. This process and the UDIC-Rheinau process played an important role in developing a market for xylose. Unfortunately, it was discovered that xylose could cause cataracts after consumption by humans, which resulted in faltering production.

There are other processes operating for instance with acid gas such as HCl, as is the case in the Prodor process. The Héreng process uses hydrochloric acid at a concentration of 30% at ambient temperature. In the Shin-Nippon-Chisso process, HCl is used as well in varying concentrations from stage to stage.

Most of these processes have been devised to produce alcohol and yeast from glucose. However, with the advent of synthetic alcohol, produced from ethylene, wood saccharification was unable to compete.

It must, however, be remembered that an average of about 20 million tons per year of hemicelluloses are wasted in the U.S.A. and Canada. Hemicelluloses are extracted during the pulping operation, and then they are either drained or burned with the black liquor. Either way of discarding this otherwise useful raw material is not justified. If drained, wood sugars are reducing the oxygen content of water which does harm to marine life. If burned, the hemicelluloses, having only 40% carbon content, require additional fuel in contrast to lignin with at least 60% carbon which has a higher heating value.

THE "SILVICHEM" PREHYDROLYSIS PROCESS

To find an economic way of recovering hemicellulose-based sugars from wood, a mild prehydrolysis process was developed. Since beta- and gamma-cellulose dissociate 100 times faster than alpha-cellulose, wood can be treated mildly to avoid the destruction of the fiber. The fundamentals of the process are illustrated in a
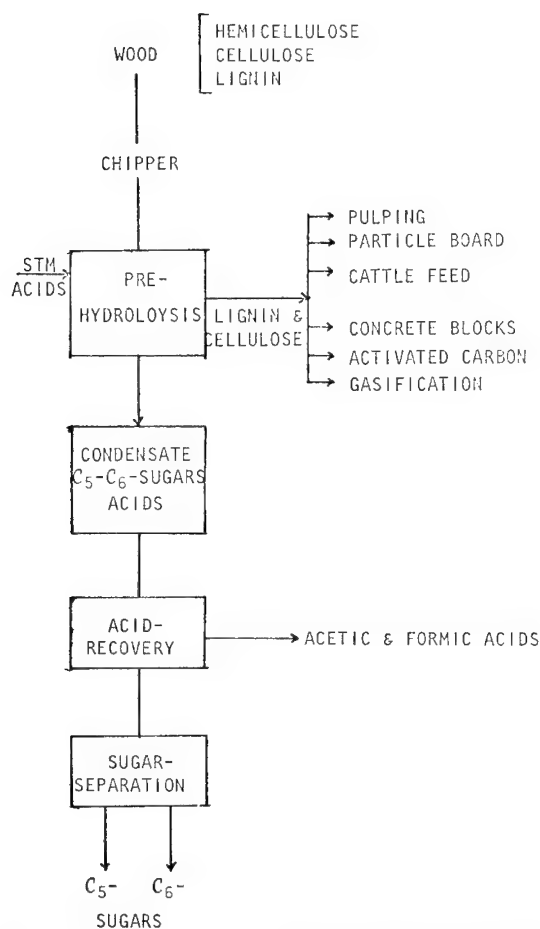
Fig. 1. Silvichem process: prehydrolysis with organic acids.

block diagram (Fig. 1). This treatment results in about 80% recovery of the hemicelluloses, mainly in the form of xylose, since the gamma-cellulose dissociates prior to the beta-component (Table II).

A patent (No. 3,523,911) was granted in the United States in August 1970, and assigned to the Silvichem Corporation of Toronto, covering this mild treatment which does not allow operating temperatures higher than 135°C to avoid the formation of furfural. Since xylose as a product is much more valuable, the retention time has to be adjusted to temperature level, particle size, pH, degree of acid mixture, and liquid-to-solid ratio. It ranges from 15 minutes to one hour, cov-

TABLE II
Cellulose Content of Wood [a]

Species	Cellulose %			Pentosan
	α	β	γ	
Western White Pine	64.6	16.3	19.1	5.3
Tan Bark Oak	56.8	20.0	23.0	22.8

[a]L. E. Wise, *Wood Chemistry,* Reinhold Publishing Corp., New York, 1944.

ering the reaction of the hydrolysis, which is exothermic, to the extent of 36 Kcal/kg.

The severe corrosion problem normally encountered with wood hydrolysis is confined to the reaction zone. Good experience was gained with Monel in this zone, while the other sections of the digester and the equipment for handling the other phases of the process can be made of stainless steel or plastic.

The organic acids participating in the reaction are vaporized and injected into the digester with steam. It is possible to recover the acids since more acids are generated than are initially injected. Because of the low temperature level in the reaction zone, the relatively short retention time and the exothermic reaction, the consumption of steam per ton of sugar is about one ton.

Xylose is unstable and it dissociates quickly at elevated temperatures. Therefore, the high-temperature saccharification processes (higher than 135°C) are not advantageous if the hemicellulose conversion and recovery as xylose is desirable. High temperatures and acid concentrations result in the destruction of xylose to furfural with corresponding deterioration of the fiber as well.

It is not economical to convert a valuable product like xylose to furfural which commands a lower price. After the mild prehydrolysis as described, the fiber will not be seriously affected. The degree of polymerization (DP) of the residual cellulose after the withdrawal of 80% of hemicellulose, was in the order of 900 with a range of viscosity between 30 and 40 centipoise. Papermakers know that hemicelluloses have an influence on the quality of paper. Some hemicellulose content is desirable in papermaking fiber. This condition is possible to achieve in a mild, well-controlled prehydrolysis. An analysis of sulfite pulp from spruce indicates 2.5% residual hemicelluloses [1]. Libby [2] shows 5.1% pentosans in unbleached sulfite pulp and 5.4% in bleached pulp. The chemical cellulose (also sulfite pulp) contains 2.9% of pentosans. Nikitin [3] states that the lower molecular weight hemicelluloses do not contribute appreciably to paper strength. The hydrolytic removal of these nonessential hemicelluloses (gamma-cellulose and in part beta-cellulose) is the central idea of the present process. In a mild prehydrolysis the gamma-cellulose dissociates first, yielding mainly pentoses.

In addition to woody plants, the biomass of other plant species may also serve as a source of hemicelluloses. For example, sugarcane bagasse contains about 25% pentoses, and its less useful pith (parenchyma) tissue contains even more (30%). About 80% of the pentoses can be recovered as xylose and the bagasse fiber can be further processed as pulp.

Xylose can also be recovered from corn cobs, straw, oat shells, sunflower seed shells, coffee bean shells, etc. Most of these materials could be discarded or burned for energy recovery after xylose removal.

To check the suitability of prehydrolyzed fibrous raw material for pulp and paper manufacture a separate pulping study was initiated, employing laboratory-scale digesters. Test runs indicated that less energy was required to pulp prehydrolyzed materials than ordinary wood chips. For instance, the "H" factor, which indicates the pulping energy requirements, is 800 for wood and 300 for bagasse, but by applying a dual-stage prehydrolysis, the "H" factor drops to 20.

Another significant advantage of prehydrolysis pulping is that the spent liquor is almost entirely lignin, and that the water-to-solids ratio of the liquor is about 3:1. Thus, the energy required for concentrating the black liquor is considerably lower. The potential chemical utilization of the spent liquor may also be easier. Figure 1

TABLE III
Velocity Constants of Decomposition of Sugars at a Temperature of
180°C and a Concentration of 0.8% H_2SO_4

Type of Sugar	First Order Reaction Velocity Constant K (Minutes^{-1})	Half Life (Minutes)
D-Glucose	0.0242	28.6
D-Galactose	0.0262	26.4
D-Mannose	0.0358	19.4
D-Arabinose	0.0421	16.4
D-Xylose	0.0720	9.6

illustrates how the hemicellulose-based wood sugar-recovery prehydrolysis process may be linked with pulping or other alternative fiber-utilizing processes.

The condensate resulting from the prehydrolysis is a mixture of C_5 and C_6 components. The pentoses ($\bar{M}_w = 150.13$) may include xylose, arabinose, ribose, and lyxose. The hexoses ($\bar{M}_w = 180.16$) may include glucose, mannose, allose, altrose, talose, galactose, idose and gulose. In a mild prehydrolysis, xylose constitutes over 90% of the hydrolyzate, with glucose, mannose and galactose accounting for the rest.

There are several processes for the separation of the various sugar components in a mixture. First, the acids are removed in several steps. If organic acids are to be recovered, an evaporation step (preferably under vacuum) is required while other acids can be neutralized and withdrawn by means of ion exchange. Then the separation of C_5 and C_6 components can be carried out either by selective crystallization or by microbial conversion.

The selective crystallization again can be arranged possibly after hydrogenation. Xylitol and sorbitol may be produced by hydrogenation, since these saturated alcohols are less susceptible to dissociation and can be crystallized at lower operating costs and higher recovery rates. The hydrogenation is performed by means of a Raney nickel catalyst, which is rather sensitive so that the sugars to be treated have to be very pure. Chloride ions must be prevented from entering this reduction phase. Hoffmann-LaRoche has developed a catalyst which requires a longer retention time but higher recovery rates are possible.

The separation of C_5 and C_6 sugars can also be accomplished by means of microbial conversion. Some microbes are suitable for a selective processing of C_6 components which in turn permit the concentration of xylose and its recovery and purification.

Glucose is normally produced from polysaccharides other than hemicelluloses of wood or annual plants. However, the latter materials are the only source for pentoses, especially xylose.

D-Sorbitol has been available commercially ever since the hydrogenation of D-glucose was mastered. Sorbitol is used as a sweetener for diabetics, as a humectant, surfactant, polyol, as well as plasticizer. The largest share, however, is processed to ascorbic acid (vitamin C). Xylitol, in turn, is hardly available and known, although in many ways it is more suitable for the various end uses than

TABLE IV
Products from Hemicelluloses

Raw Material or Base	Process or Reaction	Main Product or Derivative	By-Product	Further Processing to:	Usage Of Main And By-Products
Wood	Hydrolysis	Pentoses and Hexoses	Organic Acids Cellulose Lignin	Pulping Bldg. Materials Activated Carbon Cattle Feed	Xylose: Surfactant for Printing Ink Additive to Tanning Compounds Papersizing, Cattle Feed
Xylose	With Acids	Furfurol	-	Tetrahydrofuran	Plastics
Xylose	Hydrogenation	Xylitol	-	—	Sweetener, Humectant, Surfactant
				Xyphthalic Resin	Plasticizer, Diureticum, Blood Infusion Plastics
Glucose	Hydrogenation	Sorbitol	-	Ascorbic Acid (Vitamin 'C')	Sweetener, Humectant, Surfactant Plasticizer
Xylose	Esterization	Emulsifier	-	-	Food Additive, Detergent
Xylose	Oxydation	Xylonic Acid	-	Trioxy Glutaric Acid	Binder Sequestering Agent for Detergents
Xylose	Double Bond Oxydation	Trioxy Glutaric Acid	-		
Xylose	Methylation	Methyxyloside	-	With Isocyanide	Polyurethane
Glucose		α Methyl Glucoside	-	With Isocyanide	Polyurethane
Xylose	Oxydation	Tartaric Acid	-		
Pentoses Hexoses	Industrial Fermentation	Adenylic Acid, Inosonic Acid, Citric Acid, Kusic Acid, Guanylic Acid, L-Malic Acid, Oxalic Acid, Penicillin, Polysaccharide Gums, Pyruvic Acid, D-Erythritol, Fumaric Acid, Gluconic Acid, Glutamic Acid, Monosodium Glutamate, Levulinic Acid, D-Tartaric Acid, Vitamin B_{12}, Enzymes, Yeast, Alcohol, Steroids, Proteins, Etc.			

sorbital. It is sweeter, does not cause cavities, is used as a component for blood infusions to avoid shock after surgery, and for parenteral feeding. It also can be used as a plasticizer, polyol, diureticum and a humectant in cosmetics, etc.

Xylose as a monomer also lends itself to processing for derivatives other than xylitol. It can be esterified to make an effective emulsifier which can dissolve oil in water at a ratio of 200:1; it can be oxidized to xylonic acid with one carboxy radical and to trioxyglutaric acid by forming two carboxy radicals. The trioxyglutaric acid can be used as a chelating agent to replace tartaric acid and citric acid. Xylose can be methylated to form methyl xyloside which in turn reacts with isocyanides to give polyurethane. Table IV illustrates a large spectrum of products based on xylose and glucose. Industrial fermentation can give a great variety of derivative compounds. Some enzymes grow only on xylose and are not producible by other means.

Biochemistry has made remarkable progress in the last few decades. What appeared to be impossible only a few years ago can now be achieved with ease. For instance, in the use of wood sugars as nutrients for microbes, great progress has been made. In the early days the concentration of sugars had to be in the range of 3 to 3.5%, but now the microbes will attack concentrations as high as 60%. Originally it was believed that pentoses could not be fermented to yeast, but it is now possible to accomplish this. As a matter of fact, it should be possible to make protein from bagasse (about 10% based on dry substance) and then utilize the extracted fiber for pulping or chipboard or even cattlefeed. This would not only help the hungry nations, but would also permit the establishment of new industries. Microbes build protein 10,000 times faster than animals, in the form of meat, although some essential proteins would have to be supplemented to those produced from fermentation.

CONCLUSION

The prehydrolysis process described here may be used on waste wood, as demonstrated in a pilot plant for the production of sugars and other by products. The prehydrolysis may also be a preliminary stage, preceding regular pulping operations. Sugars (mainly xylose and glucose) can be produced at low operating costs. Since wood sugars are an abundant and renewable resource, the pulp and paper industry and the chemical industry will benefit from their assured long-term supply.

The prehydrolytic treatment of wood permits substantial energy saving in pulping and will minimize problems of pollution and waste associated with chemical pulping processes. The derivation and marketing of wood sugar-based products can significantly enhance the profitability of the forest products industries.

REFERENCES

[1] M. Oshima, *Wood Chemistry, Process Engineering Aspects,* Chemical Process Monograph No. 11, Noyes Development Corp., 1965.

[2] C. E. Libby (Ed.), *Pulp and Paper Science and Technology, Vol. 1, Pulp,* McGraw-Hill Book Co., New York, Toronto, London, 1962.

[3] N. I. Nikitin, *Die Chemie Des Holzes,* Akademie Verlag, Berlin, 1955. (Moskau, Leningrad, 1951.)

[4] K. Kürschner, *Chemie Des Holzes,* Technischer Verlag, Herbert Cram, Berlin, 1966.

[5] K. Freudenberg, *Organische Chemie.* Lambert Schneider Verlag, Heidelberg, 1947.

[6] Gläser, Flügge, Scholler, and Praetorius, *Chemische Technologie Des Holzes,* Carl Hanser Verlag, München, 1954.

[7] A. J. Stamm, *Wood and Cellulose Science,* The Ronald Press Co., New York, 1964.

[8] M. Wayman, *Guide for Planning Pulp and Paper Enterprises.* FAO Forestry and Forest Product Studies No. 18. Food and Agricultural Organization of the United Nations, Rome, 1973.

[9] H. F. Funk, et al., U.S. Patent No. 3,523,911, Aug. 11, 1970. Method of Separating Components of Cellulosic Material.

[10] T. E. Gieruszczak. Biomass: Energy Source of the Future?, *Engineering Digest, 21* (1), (1975). Canadian Engineering Publications Ltd., Toronto.

[11] M. Wells, *What Your House Will Be Like in Fifty Years.* Mainliner (United Airlines), Sept. 1974.

[12] E. E. Harris and A. A. Kline, *Physical and Colloidal Chemistry,* 1949, vol. 53, p. 344.

[13] T. Kobayashi, Wood Hydrolysis and Fermentation Process, *Biochemistry,* (1971).

[14] K. Lang, Xylit, Stoffwechsel Und Klinischz Verwendung (Xylitol, Metabolism and Clinical Usage). *Klin. Wochenschrift 49,* 233–45 (1971).

INDUSTRIAL PYROLYSIS OF CELLULOSIC MATERIALS

FRED SHAFIZADEH

Wood Chemistry Laboratory,
Department of Chemistry and School of Forestry,
University of Montana,
Missoula, Montana 59801

SYNOPSIS

Industrial pyrolysis of cellulosic materials to various fuels and chemicals requires an understanding of the complex reactions involved and how they can be controlled to provide acceptable yields. Investigation of a variety of model compounds and cellulosic substrates by modern methods of thermal and chemical analysis has shown that initial pyrolysis of glycosidically linked compounds takes place through transglycosylation to provide a mixture of anhydro sugars and randomly linked oligosaccharides. At higher temperatures, dehydration, fission and rearrangement of the sugar units provide a volatile fraction containing water and various carbonyl compounds. These reactions are also accompanied by evolution of carbon dioxide and carbon monoxide. The residues which could not escape the heated zone are carbonized by further dehydration, condensation of the unsaturated products, elimination of the substituent and crosslinking of the resulting free radicals. Since the initial pyrolytic reactions are heterolytic, the course of the pyrolysis and the yield of various products could be substantially changed by addition of acidic or alkaline catalysts.

INTRODUCTION

Chemical utilization of cellulosic materials, for products other than pulp and paper, involves breakdown of the substrate by biological, chemical or pyrolytic methods. Each of these methods offers certain advantages and disadvantages that should be evaluated in terms of the available raw material and the desired product.

Thermal degradation or destructive distillation has a long industrial history [1-6] dating back to the ancient Chinese and Egyptians who used the tarry products for embalming. Recently, it was used to obtain several products, including charcoal, acetic acid, wood alcohol and tar. The traditional pyrolytic methods could be divided into three industrial categories: carbonization to obtain charcoal (or activated carbon) without recovery of the by-products; carbonization of hardwood to provide charcoal and pyroligneous acid, from which acetic acid and methanol can be recovered as the main products; and carbonization of resinous softwoods to produce charcoal, turpentine and pine tars. In all these methods, break-

153

down of the cellulose or the sugar units to volatile pyrolysis products is suppressed in order to produce more char. Consequently, the yield of other compounds is relatively small.

In comparison with the saccharification processes, the pyrolytic methods offer the advantages of rapid rate of reaction and avoiding large volumes of water, acid, alkali and expensive corrosion-resistant reactors. The major disadvantage, however, is the combination of unspecific reactions which give a large number of products in low yields. Consequently, revival of a competitive pyrolysis industry depends on application of fluidized bed and other engineering technology for rapid heating and processing and understanding the mechanism of the reactions involved so that they could be controlled or catalyzed to provide better yields.

The pyrolysis products of cellulosic materials could be collected as char, tar and volatile fractions. This article provides an analysis of these fractions and the chemical reactions which are responsible for their production. At high temperatures, sufficient energy is available to produce a series of consecutive and concurrent reactions which, if allowed to continue, provide interactable mixtures [1]. By using a variety of model compounds and application of new methods of thermal and chemical analysis, it has been possible to unravel the complex pyrolytic transformation. These transformations could be divided into four categories. At the earlier stages of heating the carbohydrate molecules display loss of absorbed water [7], breakage of hydrogen bonds [8,9], increased heat capacity and phase change [7-12]. On further heating they show anomerization [13], transglycosylation, or the cleavage of the glycosidic groups and polymerization of the sugar units, which are mainly responsible for the tar fraction. The transglycosylation reactions are accompanied or followed by decomposition of the sugar units through dehydration, fission and disproportionation reactions, which provide the volatile fraction including carbon dioxide and other gaseous products. Finally, condensation of the fragmentation or decomposition products, loss of substituents and free-radical interactions lead to production of a carbonaceous residue.

A discussion of the physical transformations is beyond the scope of this article, which is concerned with the chemical reactions and products.

RESULTS AND DISCUSSION

Transglycosylation and Tar Formation

Pyrolysis of a glycosidic compound as shown in Scheme I, starts with cleavage
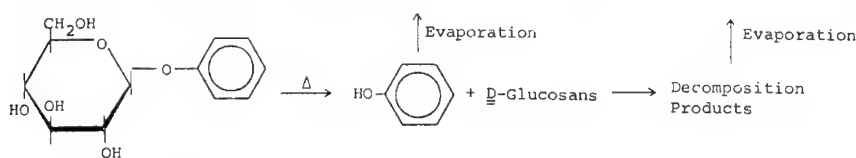
Scheme I. Pyrolytic reactions of phenyl β-D-glucopyranoside.

of the glycosidic group and condensation of the sugar moiety, which is decomposed on further heating. The sequence of these reactions as a function of temperature could be determined by thermogravimetry (TG) [11–14] and differential thermal analysis (DTA) as shown for phenyl β-D-glucopyranoside in Figure 1. The individual reactions which take place within each thermal event, characterized by
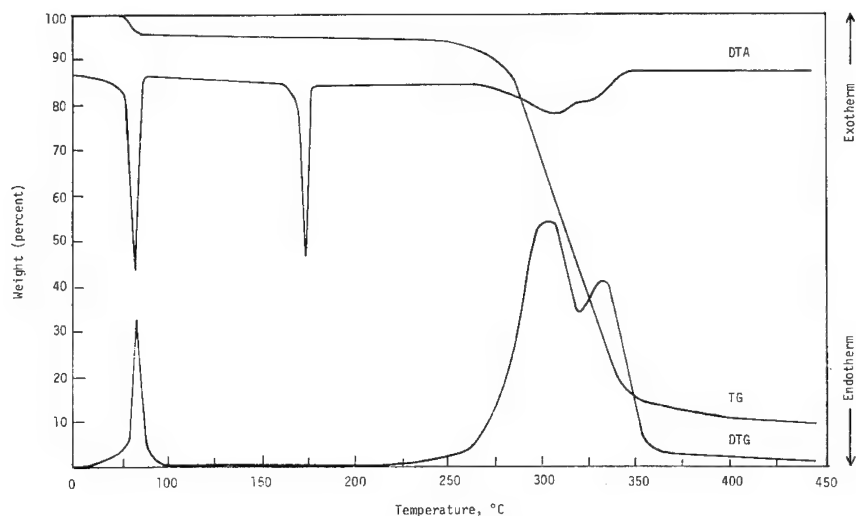
FIG. 1. Thermal analysis of phenyl β-D-glucopyranoside.

changes in mass (TG) and/or energy (DTA), are then followed by various scanning or isothermal analytical methods. In Scheme I, cleavage of the phenolic group is established by quantitative recovery of the free phenol and condensation of the sugar unit is established by recovery and chemical analysis of intermediate pyrolysis products [14,15].

It has been shown that the reaction proceeds through a heterolytic mechanism, because it is influenced by variation of the electron density produced through the introduction of various substituents on the aglycone [12-14]. This conclusion eliminated the possibility of a homolytic mechanism (free-radical cleavage of the glycosidic bond), although further breakdown and charring of the sugar units involve free-radical formation. It also indicated that the thermolysis, as a heterolytic process, must be sensitive to the effect of acidic and alkaline reagents.

Investigation of a variety of glycosides containing deoxy, amino and acetamido groups and the corresponding fully acetylated compounds [16] showed that the substituent on the sugar moiety, in addition to the inductive effect on the glycosidic bond, changes the availability and reactivity of the transglycosylation sites, and the acetylated compounds are considerably more stable than the parent compounds with free hydroxyl groups. These data [16] and production of randomly linked condensation products [14,15] confirmed that the heterolytic cleavage of existing glycosidic bonds proceeds through a transglycosylation process involving nucleophilic displacement of the glycosidic groups by one of the free hydroxyl or amino groups of the sugar molecule. Thermolysis of levoglucosan (1,6-anhydro-β-D-glucopyranose) [17], reducing and nonreducing disaccharides [18] (cellobiose and trehalose), cellulose [17] and xylan [19] and the isolation and structural investigation of the products showed that the transglycosylation reactions give mixtures of anhydro sugars and randomly linked oligosaccharides.

Dynamic thermal analysis of cellulose (Fig. 2) showed that the pyrolysis starts at $\sim$ 300°C and proceeds rapidly until most of the compound has evaporated. Isothermal investigation of this process at 300°C showed that the initial transglycosylation reactions result in depolymerization of cellulose and production of tarry materials. Gas liquid chromatography (GLC) of this fraction (Fig. 3) indicated
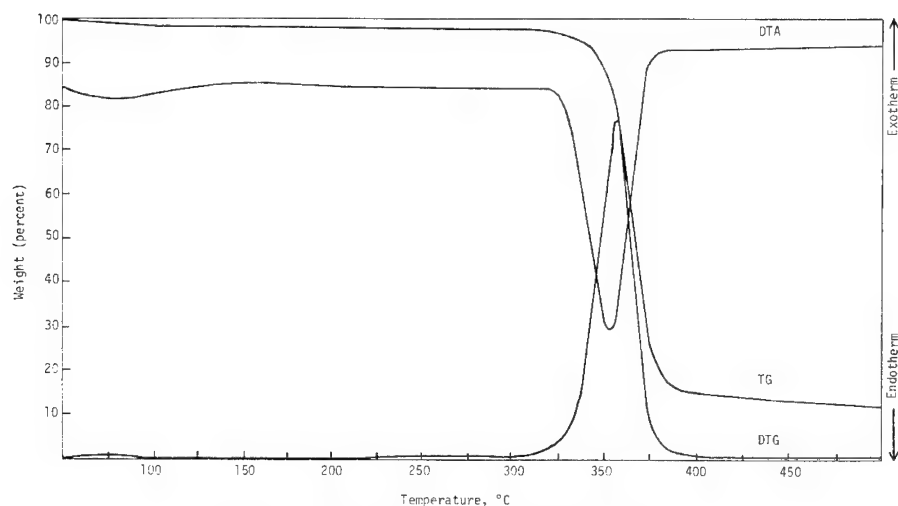
FIG. 2. Thermal analysis of untreated cellulose.

the presence of levoglucosan, a related ring isomer, 1,6-anhydro-β-D-glucofuranose, traces of α- and β-D-glucose, 3-deoxy-D-*erythro*-hexosulose, other dehydration products of D-glucose and a variety of poly- and oligosaccharides [17]. The yield of tar and its content of levoglucosan and other materials that could be readily hydrolyzed to D-glucose have been determined under several conditions and summarized in Table I. Pyrolysis at 300°C under vacuum gave ~56% tar that consisted of 34% levoglucosan, minor amounts of its ring isomer and 21% of polymeric materials that were similar to condensation products of levoglucosan. Gel permeation chromatography, periodate oxidation and Smith degradation showed that these materials are composed of randomly linked oligosaccharides. Scheme
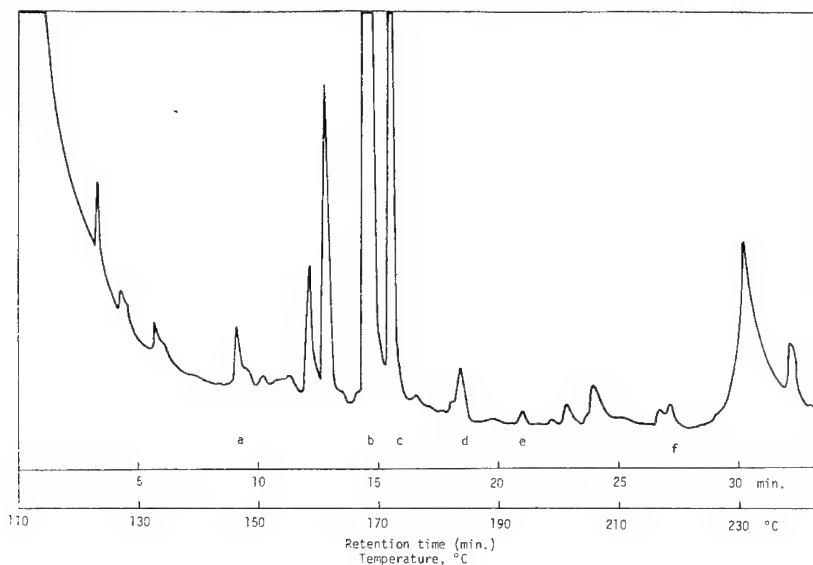
FIG. 3. Chromatogram of cellulose pyrolysis tar after reduction: (a) unknown; (b) 1,6-anhydro-β-D-glucopyranose; (c) 1,6-anhydro-β-D-glucofuranose; (d) 3-deoxyhexitols; (e) D-glucitol; (f) oligosaccharide derivatives.
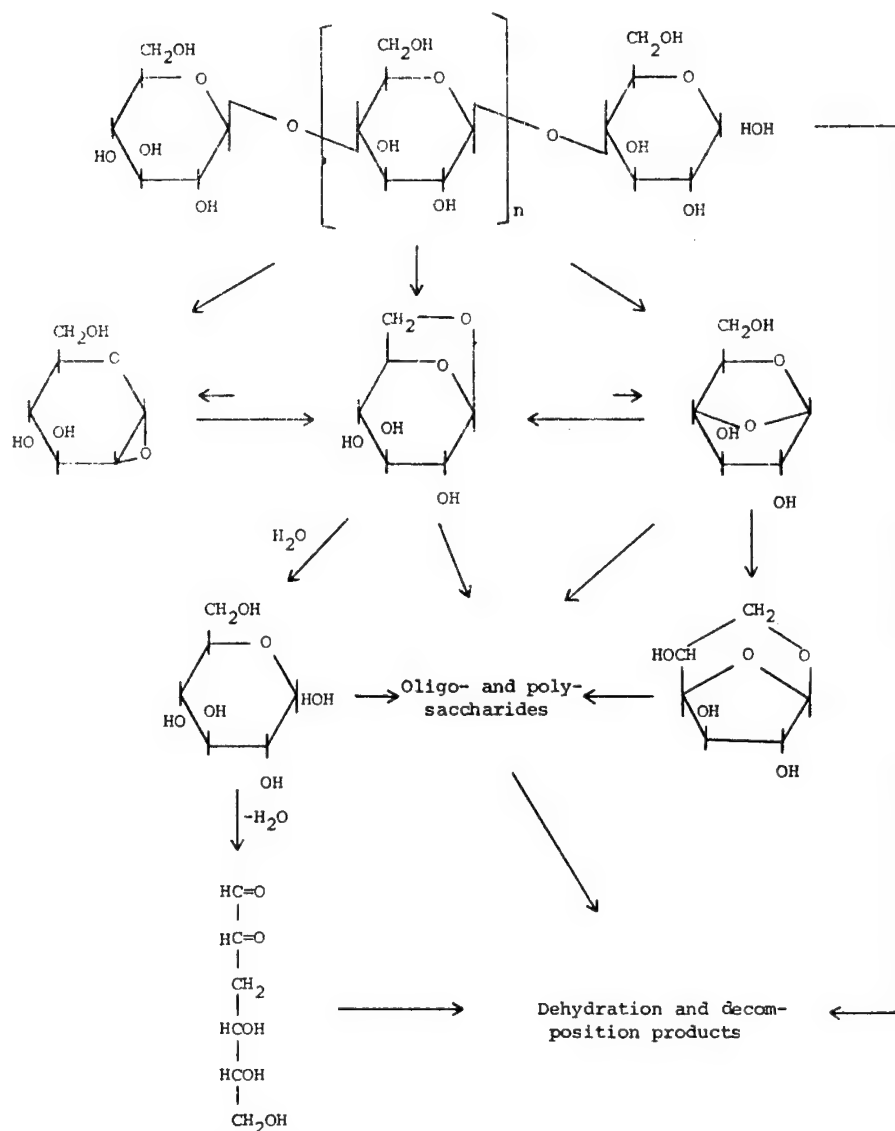
Scheme II. Pyrolysis of cellulose and transformation of the products.

II shows the transglycosylation reaction of cellulose, which accounts for the production of the above compounds.

Pyrolysis at atmospheric pressure substantially reduced the yield of the tarry products because these products could not escape from the reaction zone and were decomposed on further heating. Addition of antimony trichloride, representing an acid catalyst (Fig. 4 and Table I), lowered the temperature of pyrolysis and led to extensive dehydration and charring which is discussed later.

Pyrolysis of 4-O-methylglucuronoxylan, O-acetyl-4-O-methylglucuronoxylan, D-xylose and methyl β-D-xylopyranoside at 300° before and after addition of zinc chloride [19] gave a variety of products that were fractionated to char, tar, liquid condensate and carbon dioxide as shown in Table II. The tar fractions were further analyzed by gel permeation chromatography and Smith degradation. This

TABLE I

Analysis of the Pyrolysis Products of Cellulose at 300°C Under Nitrogen

Condition	Atm. pressure	1.5 Mm Hg	1.5 Mm Hg, 5% SbCl$_3$
Char	34.2%[a]	17.8%[a]	25.8%[a]
Tar	19.1	55.8	32.5
levoglucosan	3.57	28.1	6.68
1,6-anhydro-β-D-glucofuranose	0.38	5.6	0.91
D-glucose	trace	trace	2.68
hydrolyzable materials	6.08	20.9	11.8

[a] The percentages are based on the original amount of cellulose.

investigation showed that they contained similar oligosaccharides consisting of randomly linked D-xylose units, derived from the condensation and transglycosylation reactions.

Decomposition to Volatile Products

Because of the initial transglycosylation reaction, the volatile products obtained from cellulose, levoglucosan, glycosides and dissacharides are found to be qualitatively the same but quantitatively somewhat different [20]. The composition of degradation products could be affected by changes in the pyrolytic condition and addition of acidic or alkaline catalysts.

Analysis of the volatile products obtained on pyrolysis of levoglucosan at 600° [21] is shown in Table III. These compounds may be divided into three categories. The first category includes furan compounds, water and char, which are the expected products of the better understood acid-catalyzed dehydration reactions of carbohydrates under aqueous acid conditions [1,22]. The second category includes glyoxal, acetaldehyde and other low molecular weight carboxy compounds,
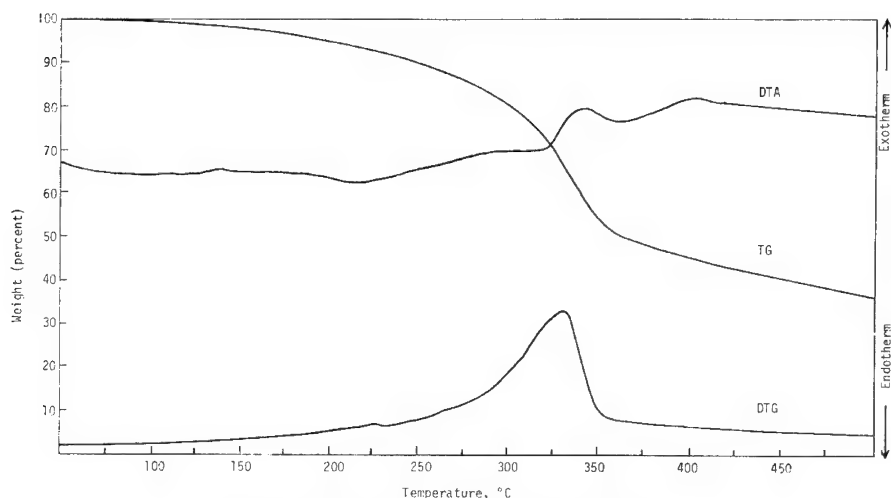
FIG. 4. Thermogram of SbCl$_3$ treated cellulose.

TABLE II
Fractionation of the Pyrolysis Products from O-Acetyl-4-O-Methylglucuronoxylan,
4-O-Methylglucuronoxylan and Model Compounds at 300°C

Product	Xylan		Acetylxylan		α-D-Xylose		Methyl β-D-Xyloside	
	Neat	+ZnCl2	Neat	+ZnCl2	Neat	+ZnCl2	Neat	+ZnCl2
Char	31.1[a]	42.2	22.1	31.2	13.8	35.2	19.7	45.4
Tar	15.7	3.2	33.1	10.0	50.2	15.2	45.0	4.0
Liquid Condensate	30.6	45.3	27.0	40.0	13.1	25.3	16.2	27.9
Carbon dioxide	7.9	7.5	7.5	6.3	1.0	1.2	12.5	12.6

[a] Based on the weight of the sample.

which are similar to the alkaline-catalyzed fission products of the sugar molecule formed through the reverse aldol condensation mechanism. The products formed through these pathways are further randomized by disproportionation, decarboxylation, and decarbonylation reactions to provide a third category which is characteristic for the pyrolytic reactions, especially at the elevated temperatures. In the absence of acidic or alkaline catalysts, both fission and dehydration products are formed. However, as expected, addition of these catalysts promotes the formation of one type of product at the expense of the other [21].

The chemical reactions involved were further investigated by the synthesis of le-

TABLE III
Pyrolysis Products of 1,6-Anhydro-β-D-Glucopyranose at 600°C

Pyrolysis product	Yield		
	Neat	+ZnCl2	+NaOH
Acetaldehyde	1.1	0.3	7.3
Furan	1.0	1.3	1.6
Acrolein	1.7	<0.1	2.6
Methanol	0.3	0.4	0.7
2,3-Butanedione	0.5	0.8	1.6
2-Butenal	0.7	0.2	2.2
1-Hydroxy-2-propanone	0.8	<0.1	1.1
Glyoxal	1.4	<0.1	4.9
Acetic acid	1.7	0.7	1.5
2-Furaldehyde	0.9	3.0	0.4
5-Methyl-2-furaldehyde	0.1	0.3	--
Carbon dioxide	2.9	6.8	5.7
Water	8.7	20.1	14.1
Char	3.9	29.0	16.0
Balance (tar)	74.3	36.8	40.3

TABLE IV

Percentage of the Pyrolysis Products Traced to the Labeled Carbons of
1,6-Anhydro-β-D-Glucopyranose

Compound	Neat			5% NaOH			5% ZnCl$_2$		
	1-^{14}C	2-^{14}C	6-^{14}C	1-^{14}C	2-^{14}C	6-^{14}C	1-^{14}C	2-^{14}C	6-^{14}C
2-Furaldehyde	60.8	103.4	35.8	30.2	100.7	73.0	86.0	95.8	16.6
2,3-buanedione	24.8	54.6	31.3	16.5	31.0	56.5	64.8	57.7	26.9
Pyruvaldehyde	27.3	26.3	19.1	23.3	42.0	30.7	49.7	46.7	29.6
Acetaldehyde	10.1	30.5	36.0	6.3	29.2	55.1	4.4	7.3	29.8
Glyoxal	15.4	19.2	6.9	25.5	48.3	36.0	29.5	28.2	28.2
Carbon dioxide	34.3	24.5	6.3	31.2	17.7	8.9	43.7	33.3	9.5
Carbon monoxide	21.1	18.9	16.8	38.4	18.0	13.7	36.7	27.6	11.4

voglucosan labeled at C1, C2, and C6 and tracing of the major pyrolysis products to the original positions of the sugar molecule [23]. The resulting data shown in Table IV indicate the major dehydration and fission pathways shown in Schemes III and IV [23]. These schemes are more complex and less specific than the single pathways generally postulated for normal reactions, because at high temperatures, the energy barrier becomes less significant and the thermal decomposition could proceed through different routes [1].

Dehydration

The above data indicated that 3-deoxy-D-hexosulose, which is the initial dehydration product of hexoses, plays a significant role as an intermediate in the production of furan derivatives. Isomers of this compound have been identified among the pyrolysis products of cellulose [17], D-glucose, D-fructose and D-xylose [24]. Moreover, the oligosaccharides formed from the pyrolytic transglycosylation of carbohydrate derivatives or the condensation of the reducing sugars often show UV and IR absorption bands that could be due to the presence of 3-deoxy-hexosulose units or its tautomeric forms [18,19].

In view of the above considerations, pyrolytic reactions of 3-deoxy-D-*erythro*-hexosulose (3-deoxy-glucosulose) were investigated with dynamic thermal analysis and parallel chemical methods in order to gain better understanding of the dehydration, rearrangement, decarboxylation and charring, which could ensue after the initial formation of this compound. The resulting data [25] showed that 3-deoxy-D-*erythro*-hexosulose decomposes rapidly within the range of 100–200°C (Fig. 5) as compared to D-glucose [26], levoglucosan [12] and glycosides [13,14] which decompose at the much higher temperatures of 250–350°C. Within this range, a small fraction of the compound gives 5-hydroxymethyl-2-furaldehyde, pyruvaldehyde, glycoaldehyde, glyceraldehyde and glucometasaccharinic acid as monomeric products of dehydration, fission and rearrangement; while most of the compound undergoes condensation as discussed later.

Heating at higher temperatures results in charring of the condensation products and further rearrangement and disproportionation of the initial dehydration and fission products. As shown in Table V, pyrolysis of the neat sample at 550°C gives about 10% organic volatile products, 38% of char, 18.5% of water, 12.5% of carbon dioxide and 4% of carbon monoxide. The balance of 17% is accounted for by a tar fraction. The volatile products consisted mainly of furan derivatives, including 2-furaldehyde, 2-methylfuran, 5-methyl-2-furaldehyde, 2-furfuryl alcohol
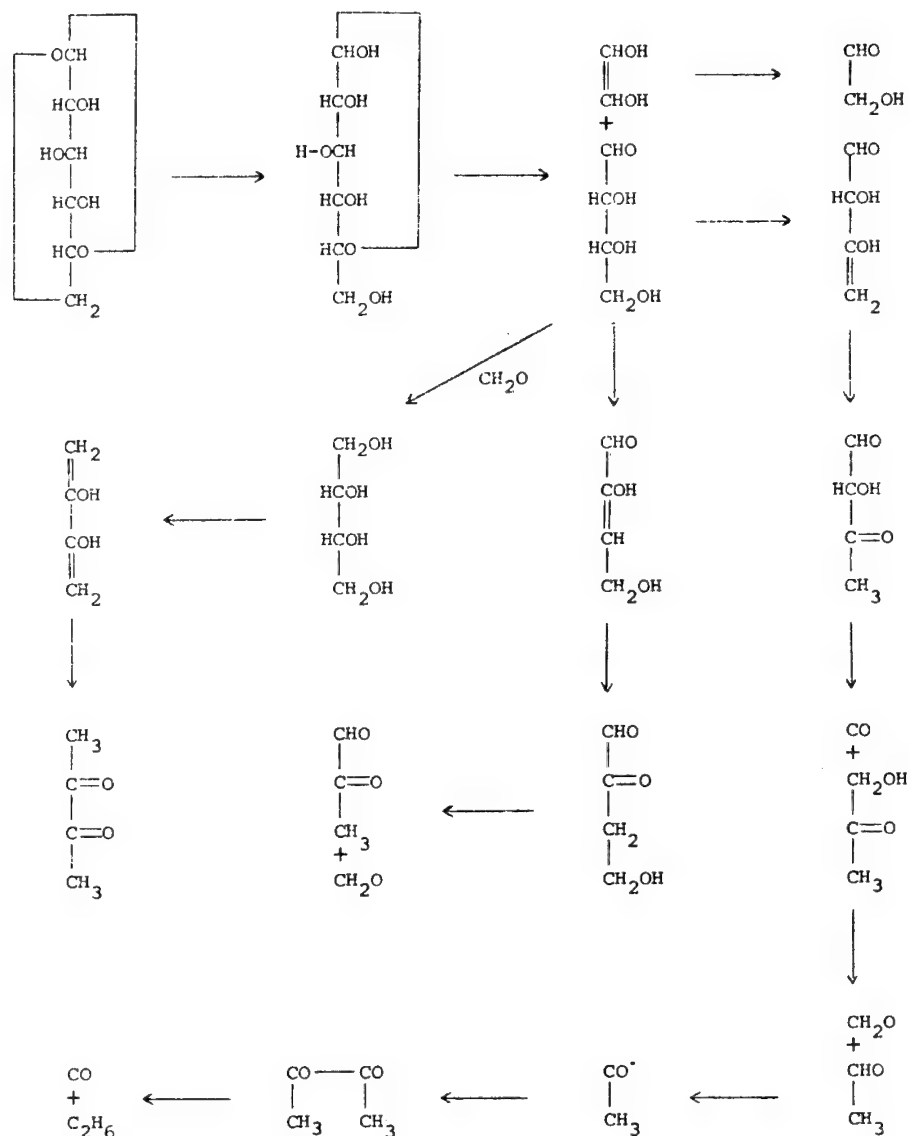
Scheme III. Degradation of levoglucosan to volatile products.

and furan, which in conjunction with water and char, indicate the preponderance of dehydration reactions. Formation of the dehydration products was further enhanced with the addition of zinc chloride. The volatile fraction also contained small amounts of acetaldehyde, propenal, 2-butenal, 1-hydroxy-2-propanone, glyoxal and carbon monoxide. Production of these compounds, considered as fission products, were increased by the addition of sodium carbonate. The above concurrent and consecutive reactions have been summarized in Scheme V.

Controlled pyrolysis of cellulose and levoglucosan provides small amounts of levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) as another dehydration product. Production of this compound, shown in Scheme VI, is greatly enhanced by addition of small amounts of acidic catalysts. However, as shown in Figure 6, the yields are reduced by further heating due to decomposition of the product [27].

TABLE V

Products of the Pyrolysis of 3-Deoxy-D-*erythro*-Hexosulose at 500°C

Pyrolysis Product	Yield (%)		
	Neat	+ZnCl$_2$	+Na$_2$CO$_3$
Acetaldehyde	1.5	0.5	2.1
Furan	0.6	0.2	0.5
Acrylaldehyde	T^a	T	0.6
2-Methylfuran	2.0	5.8	1.1
2,3-Butanedione	T	T	1.3
2-Butenal	0.8	0.4	1.0
1-Hydroxy-2-propanone Glyoxal	0.8	0.1	2.6
Acetic acid	0.2	0.1	0.6
2-Furaldehyde	3.1	6.5	0.1
5-Methyl-2-furaldehyde	0.8	0.9	0.6
2-Furfuryl alcohol	0.1	T	T
Carbon monoxide	4.0	3.3	4.4
Carbon dioxide	12.4	8.1	16.1
Water	18.4	22.3	16.8
Char	38.2	45.1	35.2
Balance (tar)	17.1	6.7	17.0
Composition of the tar after sodium borohydride reduction	(65.0)^b		
3-Deoxy-D-hexitols	(24.7)		
Glycerol	(8.3)		
3,6-Anhydro-D-glucose	(2.6)		
2-Deoxy-D-*erythro*-pentitol	(1.3)		
2,5-Dihydroxymethylfuran	(0.5)		
Glucometasaccharinic acid 1,4-lactone	(T)		
3,6-Anhydro-D-glucitol	(T)		

^{a} T = trace amounts.

^{b} Numbers in parentheses are percentages of the tar fraction.

derived from dehydration of xylose units. Formation of the latter compound was substantially increased by addition of an acidic catalyst and was reduced in the presence of alkali. These data indicate the significance of acetyl xylan in destructive distillation of hardwoods and production of wood alcohol and acetic acid from the pyroligneous acid fraction.

The dehydration and fission reactions may be understood by relating to the acid- and alkali-catalyzed decomposition of carbohydrates in aqueous solutions.
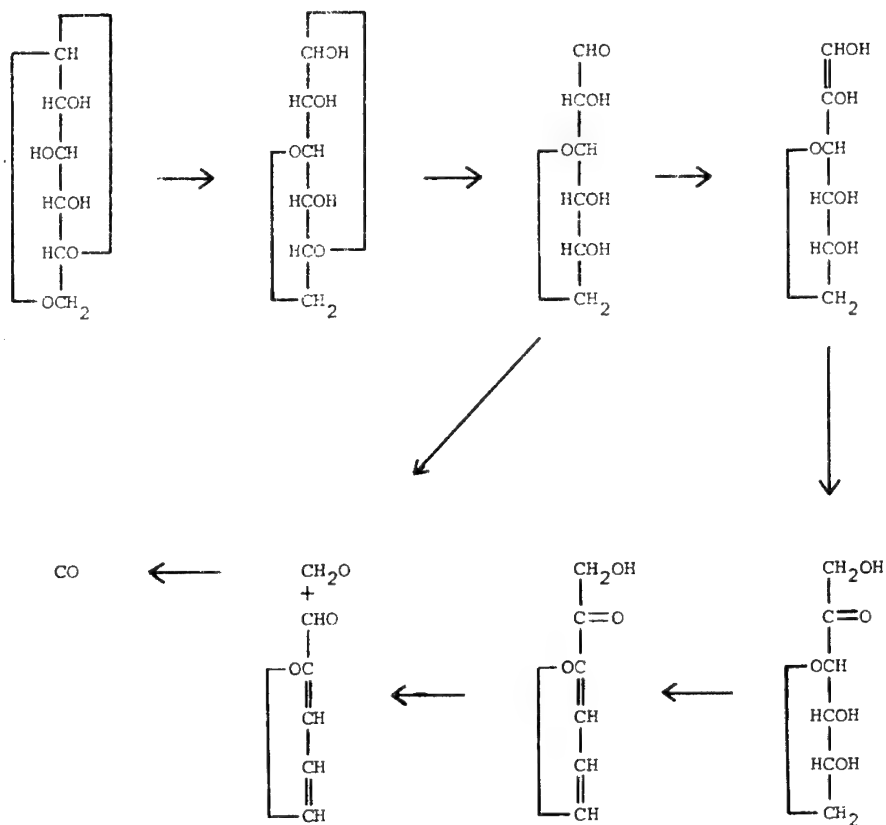
Scheme IV. Production of 2-furaldehyde under alkaline conditions.

The decomposition reactions also involve elimination of ether and ester groups. Consequently, pyrolysis of 4-O-methylglucuronoxylan (xylan) and O-acetyl-4-O-methylglucuronoxylan (acetyl xylan) at 500°C (Table VI) provides mainly acetic acid and methanol derived from the acetyl and methoxyl groups and 2-furaldehyde
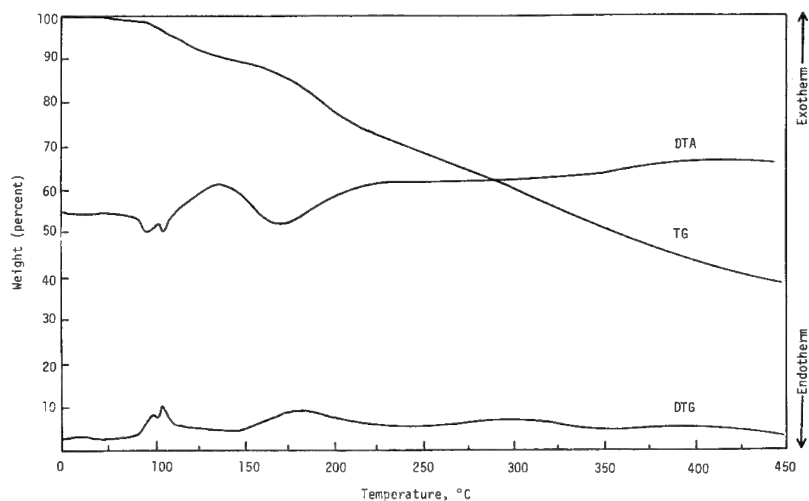
FIG. 5. Thermal analysis of 3-deoxy-D-$erythro$-hexosulose.

Condensation Products and Char
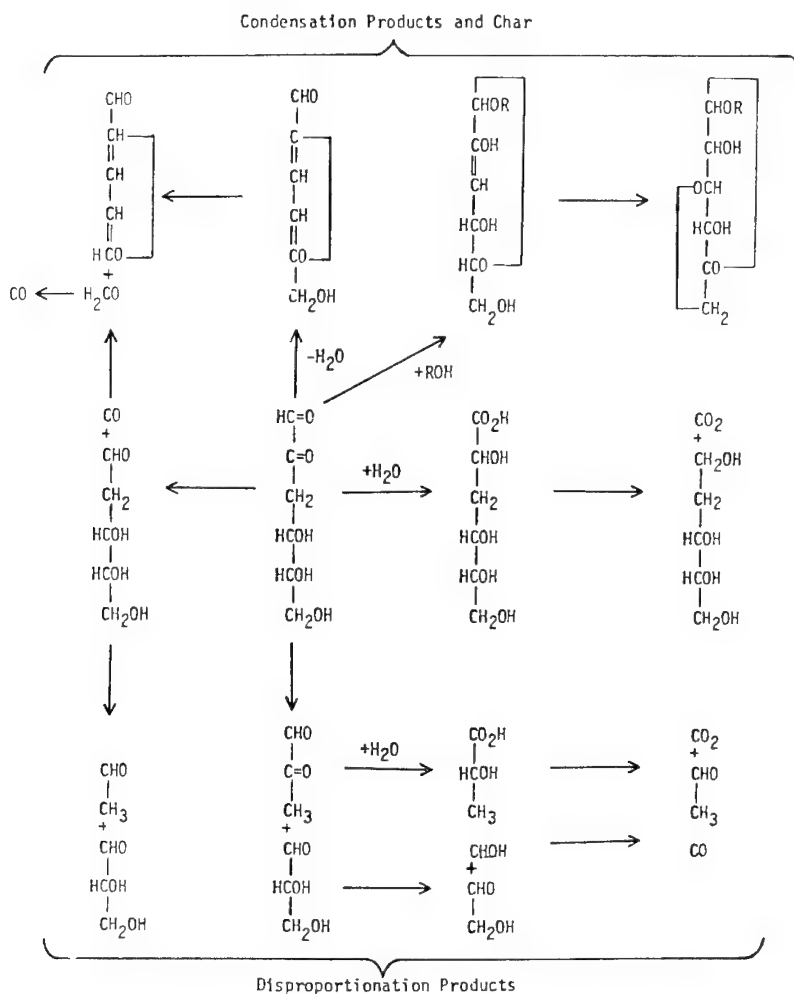
Scheme V. The pyrolytic reactions of 3-deoxy-D-*erythro*-hexosulose.

The disproportionation reactions and formation of carbon dioxide, however, are more complex and require further consideration.

Decarboxylation

Pyrolysis of cellulosic materials and carbohydrates, in general, results in evolution of considerable amounts of carbon dioxide even on moderate heating. Isotopic-tracing experiments with ^{14}C labeled levoglucosan have shown that 35% of the
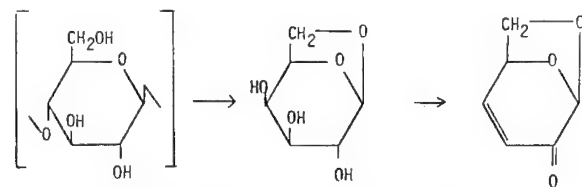
Scheme VI. Production of levoglucosenone.
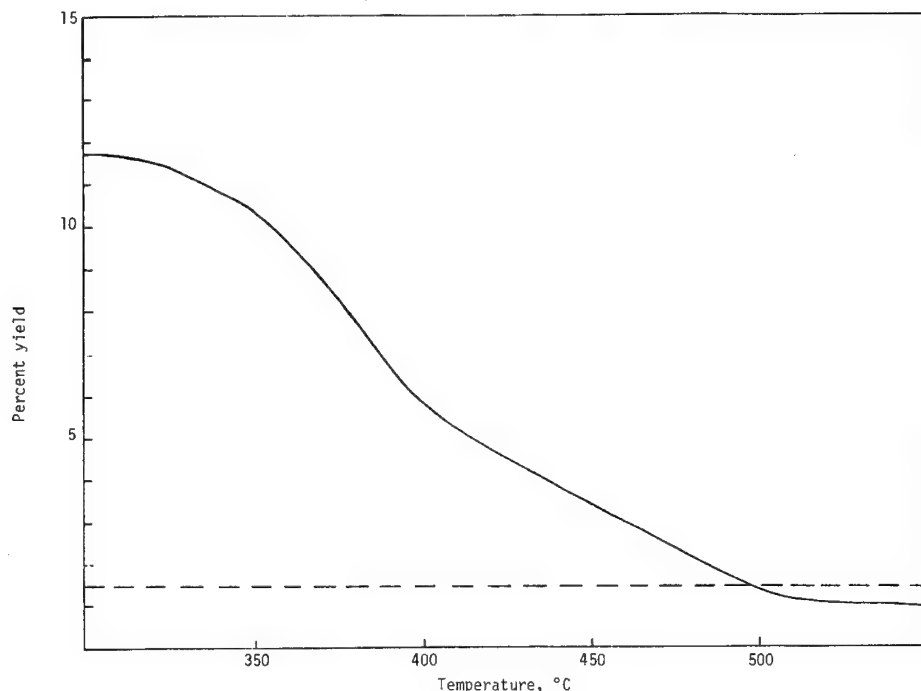
FIG. 6. Production of levoglucosenone (———) and 2-furaldehyde (- - - - -) from pyrolysis of cellulose containing 5% diphenyl phosphate.

carbon dioxide originates from C-1 of the sugar unit [23]. This amount increases to 50% or decreases to 30% when a Lewis acid or an alkali catalyst is present. The carbon dioxide could evolve from decarboxylation of carboxylic acids derived from rearrangement of the sugar unit or its carbonyl fission products. The intermediate compound may be a saccharinic acid, which is formed by dehydration and rearrangement of the sugar molecule. As noted before, one of the immediate dehydration products (3-deoxy-hexosulose) could either give furan derivatives by further dehydration or rearrange to saccharinic acids.

Carbon dioxide could also be formed from decarboxylation of 2-deoxy aldonic acids derived from a similar, but less known, dehydration and rearrangement. This rearrangement accounts for the production of 2-deoxy-D-*arabino*-hexonic acid and its lactone during the radiolysis of D-glucose [28,29].

The nature of these reactions were investigated through the pyrolysis of metasaccharinic acid (3-deoxy-D-*ribo*-hexono-1,4-lactone) and 2-deoxy-D-*arabino*-hexonic acid [29]. Heating of these compounds led to lactonization and decarboxylation. 2-Deoxy-D-*erythro*-pentitol and 1-deoxy-D-arabinitol were formed as the respective immediate decarboxylation products. The 2-deoxy lactone subsequently dehydrated by β-elimination reaction to a furanone compound (5-(2-hydroxyethylidene)-2-(5H)-furanone) and broke down to carbon monoxide, acrylaldehyde and acetic acid. The course of these reactions again was followed by dynamic thermal analysis, chemical analysis of the products, and monitoring the rate of formation of the significant products at different temperatures by mass spectroscopy. The results obtained are summarized in Table VII, Figure 7 and Scheme VII, which support the proposed theories on production of carbon dioxide.

TABLE VI

Pyrolysis of 4-*O*-Methylglycuronoxylan and *O*-Acetyl-4-*O*-Methylglucuronoxylan at 500°C

Pyrolysis Product	Xylan			Acetylxylan		
	Neat	+ZnCl$_2$	+NaOH	Neat	+ZnCl$_2$	+NaOH
Fixed gases	--	--	--	--	--	--
Acetaldehyde	2.4^c	0.1	1.6	1.0	1.9	1.6
Furan	T	2.0	0.3	2.2	3.5	0.4
Acetone	} 0.3	T	3.3	} 1.4	T	} 5.8
Propionaldehyde		T	0.7		T	
Methanol	1.3	1.0	2.1	1.0	1.0	1.8
2,3-Butanedione	T	T	T	T	T	T
Ethanol	T	--	0.6	T	--	0.6
2-Butenal	T	--	1.2	T	--	1.4
1-Hydroxy-2-propanone	0.4	T	} 2.0	0.5	T	0.8
3-Hydroxy-2-butanone	0.6	T		0.6	T	0.6
Acetic Acid	1.5	T	3.1	10.3	9.3	3.4
2-Furaldehyde	4.5	10.4	1.6	2.2	5.0	0.6
Char	10	26	21	10	23	23
Carbon dioxide	8	7	14	8	6	22
Water	7	21	26	14	15	19

TABLE VII

Products of Pyrolysis of 2-Deoxy-D-*arabino*-Hexonic Acid and the
1,4-Lactone and 3-Deoxy-D-*ribo*-Hexono-1,4-Lactone at 550°C

Product	2-Deoxy (%)				3-Deoxy-lactone (%)			
	Acid	Lactone			Neat	+ Acid	+ ZnCl$_2$	+ Na$_2$CO$_3$
		Neat	+ ZnCl$_2$	+ Na$_2$CO$_3$				
Acetaldehyde	0.5	1.8	0.9	1.1	3.4	1.6	1.2	2.6
Furan	T	0.2	T	T	1.4	0.5	1.0	0.2
Acetone	T	T	T	T	T	3.3	T	1.9
Acrylaldehyde	4.1	8.3	4.5	1.8	1.0	T	1.9	0.1
2-Methylfuran	T^a	T	1.2	0.2	0.7	1.0	0.2	0.1
2,3-Butanedione	1.3	1.8	1.2	0.6	1.8	1.5	1.8	1.4
2-Butenal	1.0	0.6	0.4	0.8	1.7	1.2	1.0	0.8
1-Hydroxy-2-propanone } Glyoxal	2.7	9.1	1.0	3.0	1.9	0.6	T	3.1
Acetic Acid	4.1	3.6	1.8	2.0	2.5	1.9	3.7	3.2
α-Angelicalactone	T	T	T	T	1.8	0.1	0.2	0.7
2-Furaldehyde	0.6	0.9	T	0.2	T	0.2	0.3	0.3
2-Furfuryl alcohol	0.2	0.3	0.1	T	1.6	1.0	1.3	0.5
β-Angelicalactone	T	T	T	T	3.6	0.3	0.4	1.4
5-(2-hydroxyethylidene)- 2(5*H*)furanone	10	14	4	3	1	<1.0	<1.0	<1.0
Carbon monoxide	5.3	3.3	2.8	3.8	3.8	8.8	7.0	6.2
Carbon dioxide	12.6	8.4	12.5	19.0	7.8	22.8	19.3	16.5
Water	26.1	17.5	19.5	16.0	8.7	10.8	17.1	16.0
Char	18.2	9.4	29.3	32.8	1.9	15.0	38.2	31.2
Tar	16.5 $_b$	25.1	17.1	10.0	62.3	22.8	4.2	8.8
2-Deoxy-lactone	(11.8)^b	(34.5)	(1.0)	(0.7)				
1-Deoxy-D-arabinitol	(2.0)	(1.1)	(0.4)	(0.5)				
3-Deoxy-lactone					(72.2)	(7.2)	(28.5)	(29.5)
2-Deoxy-D-*erythro*-pentose					(1.5)	(1.3)	(1.2)	(1.7)
2-Deoxy-D-*erythro*-pentitol					(0.5)	(0.3)	(1.1)	(1.2)

^{a} T = trace amounts.

^{b} Numbers in parentheses are percentages of the tar fraction.

FIG. 7. Evolution of CO_2, CO and H_2O on heating of 2-deoxy-D-*arabino*-hexonic acid.

Char Formation

The transglycosylation, elimination, fission and disproportionation reactions provide lower molecular weight products, which escape from the heated zone as the tar, volatile and gaseous fractions.   The remaining materials are charred and carbonized on further heating.   Production of the carbonaceous char could be enhanced at the expense of the other products by slower heating and addition of catalysts [30,31].   The charring process involves more than dehydration or elimination of the substituents on the carbon atoms of the sugar units, since such a process could lead to unsaturated volatile products and not necessarily carbonaceous residues.
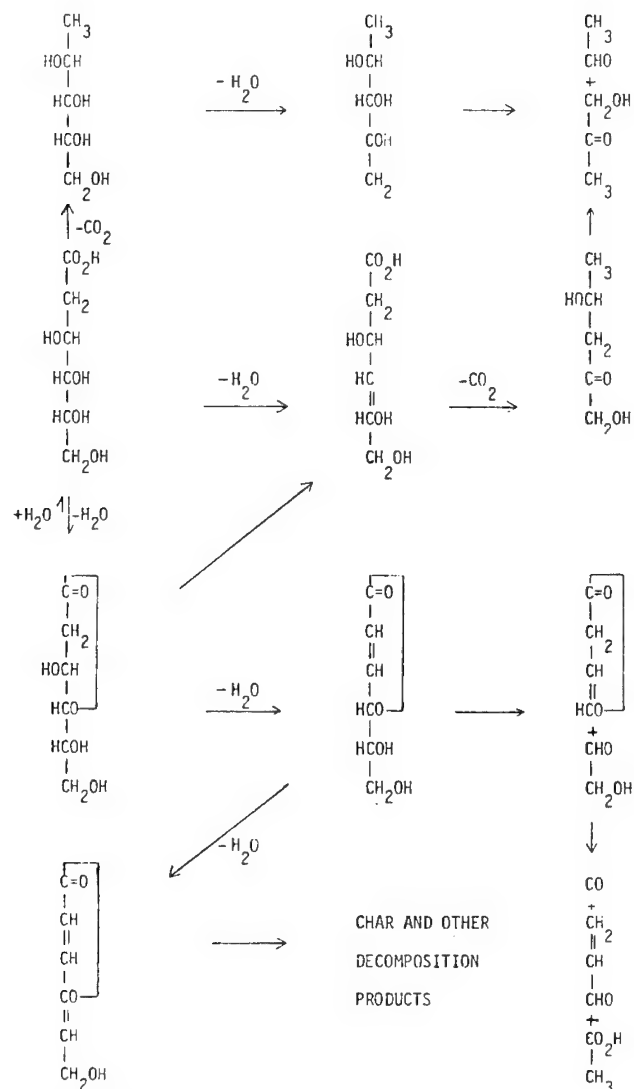
Scheme VII. Pyrolytic reactions of 2-deoxy-D-*arabino*-hexonic acid and the 1,4-lactone.

The charring reactions, which are important in flameproofing as well as the industrial pyrolysis of cellulosic material [1], have been investigated by using model compounds and various treatments or additives. These investigations have shown that the chars are produced by dehydration of the carbohydrate units, condensation of the unsaturated products to higher molecular weight materials, production of free radicals through cleavage of the carbon substituents and free-radical condensation and crosslinking, which result in carbonization of the residues [15,25].

In the normal sequence of the pyrolytic reactions, transglycosylation of carbohydrates and cellulosic materials starts at about 300°C and provides anhydro sugars and other decomposition products, which rapidly evaporate. The rate of weight loss for cellulose, determined by derivative thermogravimetry (DTG), is shown in Figure 2. The sequence of these reactions, however, could be altered by dehydration of the molecule at lower temperatures and condensation of the unsat-
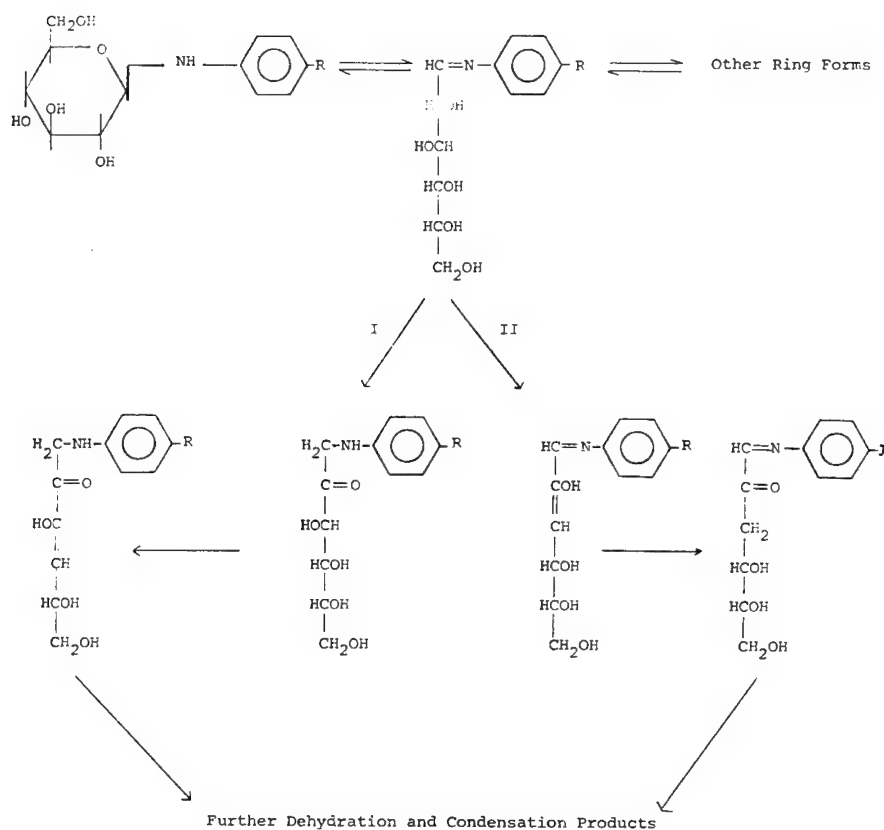
Scheme VIII. Decomposition of glycosylamines.

urated products, which are not readily evaporated or broken down to low molecu-
lar weight compounds on further heating. This effect was demonstrated by the
pyrolysis of glycosylamines (N-glycosides) and amino sugar derivatives which on
heating could form N-glycosides [32]. The N-glycosides decompose on melting at
~150–200°C by anomerization, Amadori rearrangement and β-elimination, which
is in sharp contrast with the transglycosylation and splitting of the glycosidic
group observed for O-glycosides. The resulting unsaturated products, which are
far more reactive than the normal sugars [25], then dehydrate almost quantita-
tively, and condense to provide a carbonaceous residue, as shown in Scheme VIII.

The charring process is also promoted by the addition of acid and alkali re-
agents. It was shown that the thermolysis of phenyl β-D-glucopyranoside in the
presence of 5% zinc chloride also proceeds at the lower temperature range of
150–250°C, and in two distinct stages [15]. In the first stage, the Lewis acid fa-
cilitates nucleophilic displacement of the glycosidic group and formation of ran-
domly linked and branched glucosans. These materials were quite different from
the uncatalyzed transglycosylation products and gave substantial proportions of
3,6-anhydro and furanoid structures on acid hydrolysis and Smith degradation.

In the second stage, zinc chloride catalyzes elimination of hydroxyl groups and
dehydration of the molecule. Consequently, pyrolysis of the reaction mixture at
350° and 600°C gave substantial quantities of char and water, small amounts of
carbon dioxide, tar and 2-furaldehyde and trace amounts of other dehydration

TABLE VIII
Products of the Pyrolysis of Phenyl α- or β-D-Glucopyranosides in the Presence of
Zinc Chloride at 600°C

Product	Yield (%)	
	α-	β-
2-Methylfuran	0.7	0.7
2,3-Butanedione	1.1	3.9
2-Furaldehyde	3.6	3.4
Benzofuran	0.4	0.6
"Levoglucosenone"	T	T
Carbon dioxide	6.0	5.1
Water	16.6	15.2
Char	33.5	32.6
Tar	6.8	5.4
Before acid hydrolysis		
levoglucosan	(3.6)[a]	(2.6)
phenyl D-glucopyranosides		
α-	(1.2)	(0.7)
β-		(2.7)
After acid hydrolysis		
glucose	(20.8)	(26.7)
3,6-anhydroglucose	(1.6)	(1.0)
unknown	(12)	(16)

[a]Numbers in parentheses are percentages of the tar fraction.

products. Formation of substantial proportions of char and water and only minor proportions of the volatile dehydration products (Table VIII), as well as development of ether links, indicates that zinc chloride not only catalyzes the initial dehydration reaction but also helps to condense the intermediate products to nonvolatile materials that are charred on further heating.

Condensation of the unsaturated compounds was investigated by heating of 3-deoxy-D-*erythro*-hexosulose, discussed before [25]. The polymeric materials formed at 185°C could not be completely hydrolyzed, due to nonglycosic condensation. On acid hydrolysis, they gave an insoluble product and ∼40% monomeric material, including D-glucose, 3,6-anhydro-D-glucose and the original 3-deoxy compound. The partial hydrolysis and formation of 3,6-anhydro-D-glucose and D-glucose derivatives indicate that heating not only results in elimination of the substituents (dehydration), but also effects the reverse process, namely, inter- and intramolecular addition involving the enolic double bonds.

The condensation products become progressively less hydrolyzable. A sample heated to 225°C was highly condensed and could not be hydrolyzed under acidic conditions. ESR investigation within the range of 70–280°C indicated that the initial reactions are heterolytic, but the charring of the condensation products at temperatures above 200°C, which is accompanied by a slowly proceeding weight loss (Fig. 5) involves the formation of stable free radicals. Again, this process is facilitated by the addition of zinc chloride, and the increasing intensity of the free-radical signals at higher temperatures, shown in Figure 8, is very similar to those obtained for levoglucosan [23,25]. These data show that the dehydration and condensation products, which are not broken down by heterolytic transglycosylation and reverse aldol condensation, are charred and carbonized on further heating by homolytic cleavage of the substituents and crosslinking of the carbon chain through the interaction of the free radicals, some of which remain trapped in the matrix.

Figure 4 shows the slow rate of weight loss (DTG curve) of cellulose treated
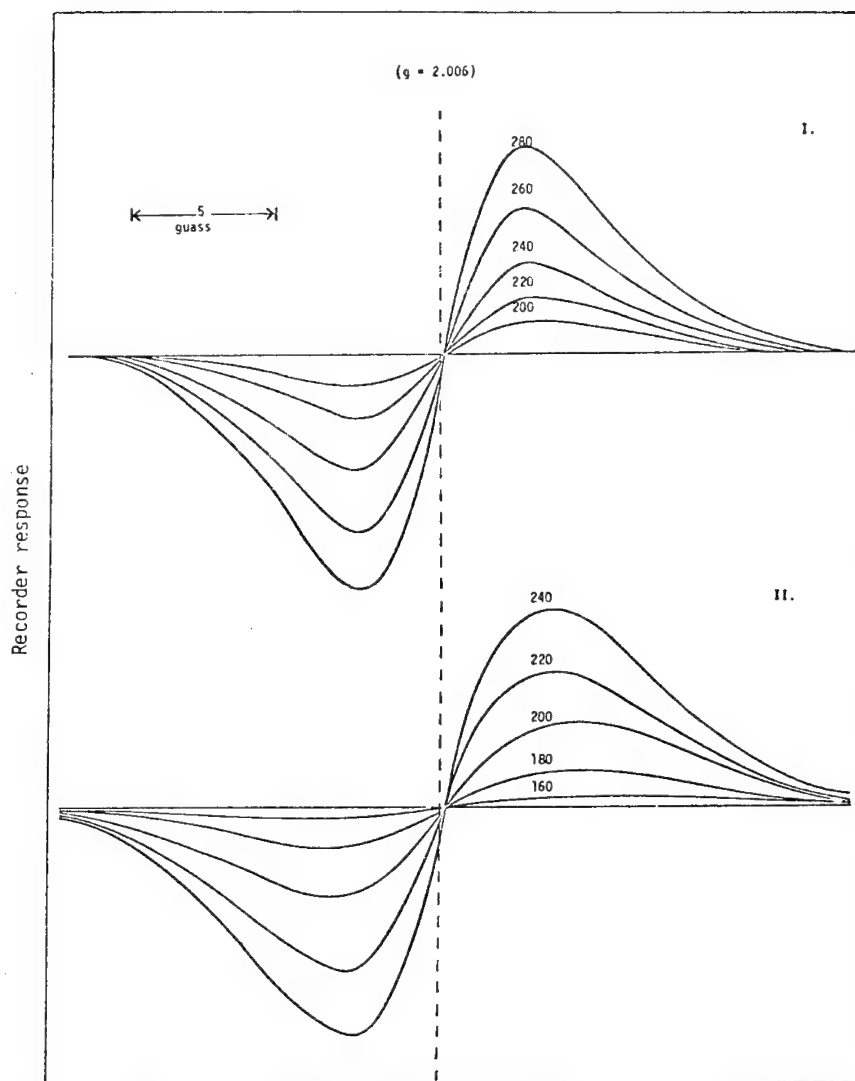
FIG. 8. ESR signals formed on heating of 3-deoxy-D-*erythro*-hexosulose in the absence (I) and presence of (II) of zinc chloride to various temperatures at the rate of ~10°C/min.

with 5% antimony trichloride over the wide range of 150–350°C, reflecting the dehydration, condensation and charring reactions, which leave ~45% of a relatively stable carbonaceous residue at 400°C (TG curve). These data are in sharp contrast with the DTG and TG curves for untreated cellulose (Fig. 2), showing a rapid rate of weight loss with a sharp peak at 350° and leaving ~15% of char at 400°C.

The effect of sodium hydroxide on charring is less pronounced and more complex. Addition of sodium hydroxide to phenyl β-D-glucopyranoside facilitates the substitution of the glycosidic group by the trans-hydroxyl group at C2 and the subsequent transglycosylation to levoglucosan [33]. It also facilitates the enolization, fission, rearrangement and charring of the sugar moiety [26]. The charred residue formed on pyrolysis of several mixtures of cellulose and sodium hydroxide at

TABLE IX

The Effect of Inorganic Compounds on Thermal Evolution Analysis of Cellulose

Flame Retardant	Evolution of Combustible Carbon				Heat Release (cal/g cellulose)[b]
	Range (°C)	Fast Rate (°C)	Max. Rate (°C)	Total at 500° (%)[a]	
H_3PO_4	200–500	200–300	275	13.9	420
$ZnCl_2$	260–500	260–500	325	23.4	820
NaOH	200–500	250–375	315	28.1	1020
$(NH_4)_2HPO_4$	210–500	250–330	305	30.9	1130
$NH_4H_2PO_4$	220–500	240–330	305	38.6	1460
Na_2CO_3	260–500	260–410	370	39.5	1490
$SbCl_3$ Hydrate	100–500	280–380	330	45.0	1720
H_3BO_3	300–500	315–425	335	55.0	2140
$NaVO_3$	200–500	275–390	345	56.4	2200
Na_3PO_4	325–410	325–410	375	59.1	2320
$CaCl_2$	285–500	285–410	355	59.6	2340
$SbCl_3$	100–500	280–380	330	60.6	2380
$NaHCO_3$	300–410	300–410	350	63.9	2520
NaCl	275–500	275–410	375	64.1	2530
$Na_2WO_4 \cdot 2H_2O$	260–425	310–410	375	66.3	2620
$(NH_4)_2SO_4$	220–500	240–380	330	66.5	2630
$NaHSO_4$	225–500	225–400	320	68.7	2720
$Na_2B_4O_7 \cdot 10H_2O$	275–500	310–400	370	69.9	2770
$NaH_2PO_4 \cdot H_2O$	275–500	275–400	340	72.5	2880
NH_4Cl	300–400	300–400	355	73.9	2940
Neat	310–390	310–390	350	76.2	3030
$(NH_4)_2CO_3$	310–410	310–390	360	76.8	3060

[a] Based on the total carbon content of the cellulose.

[b] Adjusted to 400°C.

300°C contained substantial amounts of intractable water-soluble materials, which seemed to be the sodium salt of enolic and unsaturated carboxylic compounds including 2-furoic acid. These compounds were partially precipitated when neutralized and showed a complex GLC pattern [34].

In Figures 2 and 4, the DTG curves show the rate of evolution of the combustible and noncombustible volatile products. The rate of evolution of the combustible volatile products, as a function of temperature, could be determined by thermal evolution analysis (TEA) which could be calibrated to indicate the heat content of the gassification products. Table IX shows the effect of various inorganic compounds in reducing the heat content of the gassification products or increasing the calorific value realized in the char [31]. The yield and the heat content of the char obtained from a variety of cellulosic and natural products without additives are presented in Table X [30]. This table shows that on a weight basis, the average heat value of natural fuels, 4500 cal/g, is not too far below the average heat

TABLE X
The Heat of Combustion of Natural Fuels and Their Pyrolysis Products as
Char and Combustible Volatiles

Fuel			Char		Combustible Volatiles	
Source	Type	$\Delta H^{25°}_{comb}$ (cal/g)	Yield %[a]	$\Delta H^{25°}_{comb}$ (cal/g)	Yield %[b]	$\Delta H^{25°}_{comb}$ (cal/g)
Cellulose	Filter Paper	-4143	14.9	-7052	85.1	-3634
Poplar Wood *Populus* ssp.	Excelsior	-4618	21.7	-7124	80.9	-3923
Larch Wood *Latrix occidentalis*	Heart Wood	-4650	26.7	-7169	68.5	-3732
Decomposed Douglas Fir *Pseudotsuga menzeisii*	Punky Wood	-5120	41.8	-7044	50.5	-3738
Decomposed Douglas Fir *Pseudotsuga menzeisii*	Punky Wood Fine (60 mesh)	-5373	50.0	-6871	--	-3875
Chamise *Adenostoma fasciculatum*	Stems	-4813	35.2	-6836	49.8	-3714
Ponderosa Pine *Pinus ponderosa*	Needles	-5145	37.0	-6588	61.7	-4298
Aspen *Populus tremuloides*	Foliage	-5034	37.8	-6344	59.7	-4238

[a] Heating rate 200°C/min.
[b] Heating rate 16°C/min.

values for different types of coal which range from 7915 cal/g for bituminous grade A to 3640 cal/g for lignite [35], and the comparison becomes more favored by pyrolysis to charcoal. These data indicate the potential value of the colossal amounts of cellulosic wastes and forest product residues as renewable sources of fuel and energy and also the possibilities for degassification to improve the calorific value, transportation and burning properties.

REFERENCES

[1] F. Shafizadeh, *Advan. Carbohyd. Chem., 23*, 419 (1968).
[2] H. M. Bunbury, *The Destructive Distillation of Wood*, Van Nostrand Co., New York, 1926.
[3] L. F. Hawley, *Wood Distillation*, Chemical Catalog Company, Inc., New York, 1923.
[4] M. Klar, *The Technology of Wood Distillation*, Van Nostrand Co., New York, 1925.
[5] G. Bugge, *Industrie der Holtzdestillations-Producte*, Theodor Steinkopff, Dresden and Leipzig, 1927.
[6] L. E. Wise and E. C. Jahn, *Wood Chemistry*, Reinhold Publishing Corp., New York, 1952.
[7] F. Shafizadeh and R. A. Susott, *J. Org. Chem., 38*, 3710 (1973).
[8] F. Shafizadeh, G. D. McGinnis, R. A. Susott, and C. W. Philpot, *Carbohyd. Res., 15*, 165 (1970).
[9] F. Shafizadeh, R. A. Susott, and C. R. McIntyre, *Carbohyd. Res., 41*, 351 (1975).
[10] G. W. Smith and F. Shafizadeh, *J. Chem. Soc. B*, 908 (1971).
[11] F. Shafizadeh, G. D. McGinnis, R. A. Susott, and C. W. Philpot, *Carbohyd. Res., 13*, 184 (1970).
[12] F. Shafizadeh, *J. Polym. Sci. C, 36*, 21 (1971).
[13] F. Shafizadeh, G. D. McGinnis, R. A. Susott, and H. W. Tatton, *J. Org. Chem., 36*, 2813 (1971).
[14] F. Shafizadeh, R. A. Susott, and G. D. McGinnis, *Carbohyd. Res., 22*, 63 (1972).
[15] Y. Z. Lai and F. Shafizadeh, *Carbohyd. Res., 38*, 177 (1974).

[16] F. Shafizadeh, M. H. Meshreki, and R. A. Susott, *J. Org. Chem., 38,* 1190 (1973).

[17] F. Shafizadeh and Y. L. Fu, *Carbohyd. Res., 29,* 113 (1973).

[18] F. Shafizadeh and Y. Z. Lai, *Carbohyd. Res., 31,* 57 (1973).

[19] F. Shafizadeh, G. D. McGinnis, and C. W. Philpot, *Carbohyd. Res., 25,* 23 (1972).

[20] P. S. Chin, Ph.D. Dissertation, University of Montana, 1973.

[21] F. Shafizadeh, C. W. Philpot, and N. Ostojic, *Carbohyd. Res., 16,* 279 (1971).

[22] F. Newth, *Advan. Carbohyd. Chem., 6,* 83 (1951).

[23] F. Shafizadeh and Y. Z. Lai, *J. Org. Chem., 37,* 278 (1972).

[24] K. Kato and H. Komorita, *Agr. Biol. Chem., 32,* 715 (1968).

[25] F. Shafizadeh and Y. Z. Lai, *Carbohyd. Res., 40,* 263 (1975).

[26] F. Shafizadeh and Y. Z. Lai, *Carbohyd. Res., 26,* 83 (1973).

[27] F. Shafizadeh and P. S. Chin, unpublished data.

[28] S. Kawakishi and N. Namiki, *Carbohyd. Res., 26,* 252 (1973).

[29] F. Shafizadeh and Y. Z. Lai, *Carbohyd. Res., 42,* 39 (1975).

[30] R. A. Susott, W. F. DeGroot, and F. Shafizadeh, *J. Fire and Flammability, 6,* 311 (1975).

[31] F. Shafizadeh, P. S. Chin and W. F. DeGroot, *J. Fire and Flammability, Fire Retardant Chemistry, 2,* 195, (1975).

[32] F. Shafizadeh, G. D. McGinnis, R. A. Susott, and M. H. Meshreki, *Carbohyd. Res., 33,* 191 (1974).

[33] F. Shafizadeh, Y. Z. Lai, and R. A. Susott, *Carbohyd. Res., 25,* 387 (1972).

[34] F. Shafizadeh and H. Lundstrom, unpublished data.

[35] E. W. Washborn (Ed.), *International Critical Tables, Vol. II,* McGraw-Hill Book Co., Inc., New York, 1972.

PROCESS-DEVELOPMENT STUDIES OF THE ENZYMATIC HYDROLYSIS OF NEWSPRINT

C. R. WILKE and R. D. YANG

University of California,
Berkeley, California 94720

SYNOPSIS

Background laboratory work and a tentative process for enzymatic hydrolysis of waste newsprint are described. Enzyme is produced by *Trichoderma viride* QM 9414 in a two-stage system comprising cell growth in soluble sugars and enzyme induction on solid cellulose. Recovery of enzyme from the product-sugar by adsorption on fresh plant feed and employment of cell recycle around the enzyme induction stages are important features of the process. Design studies indicate that it may be possible to produce sugars at a favorable cost, although additional research is needed to confirm a number of process assumptions.

INTRODUCTION

A tentative processing scheme for hydrolysis of waste newsprint based on laboratory data for ball-milled paper has been proposed by Wilke and Mitra [1]. Because of the high cost of ball-milling, subsequent studies have been made in this laboratory to assess the possibility of employing a less stringently milled substrate. This work has led to a modified process recently described by Wilke and Yang [2]. The present paper will review this latter work and describe a further revised process design and cost analysis based on more recent information.

It should be recognized at the outset, however, that many important features of the proposed processing method have not been fully demonstrated in the laboratory, and that a pilot-plant study of the operation will be necessary to establish the performance under realistic practical conditions. Therefore, the processing costs developed herein are primarily intended to provide perspective on important cost factors and do not necessarily represent results which can be obtained in practice. However, such cost studies are valuable as a guide to indicate potentially important areas for future study, and to ascertain that the research has at least some hope of leading to an economically feasible technology.

LABORATORY STUDIES

Newsprint in the form of copies of the Wall Street Journal was chosen as a representative raw material. This paper was found to have a reasonably consistent average composition of 61% α-cellulose, 21% lignin, and 16% hemicellulose. No adverse effects of the printing ink on hydrolysis or fungal growth have been observed.

Cellulase enzyme was prepared in batch fermentation of the fungus *Trichoderma viride* QM 9414 obtained from the Natick Laboratories [3]. Enzyme solutions of varying strength were prepared by redissolving the enzyme protein obtained by acetone precipitation. Enzyme activities were measured and defined in terms of C_1, C_x and Filter Paper units according to Mandels and Weber [4].

Sugars produced by hydrolysis were measured as total reducing sugar by the DNS method [5] and reported as glucose.

HYDROLYSIS KINETICS

Effect of Milling

Mitra and Wilke [6], following the earlier work of Ghose and Kostick [7], found that excellent levels of enzymatic hydrolysis could be obtained with newsprint which had been ball-milled to −200 mesh. However, this type of milling does not appear practical for large-scale processing because of prohibitive equipment and energy costs. To assess the possibilities of alternate milling methods, hydrolysis tests in shaken flasks were made by Rubik [8] on a variety of newsprint preparations. Table I shows the results for −325 mesh ball-milled material and several size distributions obtained with a Wiley mill. Suspensions of the newsprint of 5% or 10% concentration were contacted for 48 hr with enzyme solution of varying filter paper activity units (FPA) at 50°C. Except for the ball-milled material the percentage conversion of the cellulose to sugar was found to be independent of the particle size. Even larger particles of the paper, in the form of paper punches, showed the same conversion as equivalent suspensions of the Wiley-milled paper. Recent results of Mandels and co-workers [9] for hydrolysis of a variety of materials support this conclusion. Therefore, it was concluded that a fairly coarse level of milling could be used in large-scale processing by accepting a somewhat lesser degree of conversion than that obtained by ball-milling.

The experiments of Rubik also indicated that 5% suspensions gave a much better hydrolysis than 10% suspensions at the same initial enzyme concentration.

TABLE I.
Newsprint Hydrolysis vs. Milling-Shaken Flasks at 50°C, 48 hr

SUBSTRATE	FPA	CONVERSION
10% WILEY (−20)	4.06	24.8%
10% BALL (−325)	4.06	72.9%
5% WILEY (−20)	4.06	41.1%
5% BALL (−325)	4.06	86.1%
10% WILEY (−20)	2.70	18.0%
10% WILEY (−100)	2.70	17.0%
10% WILEY (−325)	2.70	17.2%
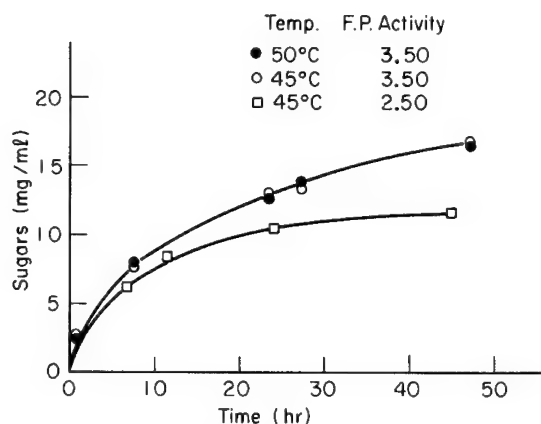
FIG. 1. Hydrolysis of 5% suspensions of −20 mesh newsprint.

Hydrolysis with Vigorous Agitation

Because of the obvious low level of mixing obtained in the shaken-flask experiments of Rubik, described above, it seemed desirable to determine the hydrolysis rates under more vigorous agitation and with larger volumes of material. Hydrolyses were conducted in 600-ml glass jars immersed in a water bath at 45°C and 50°C, and stirred with a motor-driven marine impeller at 300 rpm. Paper suspension was prepared by mixing 15 g of ground paper with 300 ml crude enzyme filtrate. Figure 1 shows the results of hydrolysis at 45°C and 50°C using 2.5 and 3.5 FPA enzyme solutions. Hydrolysis at 45°C give essentially the same conversion as at 50°C. Conversions at 36% and 52% (based on α-cellulose) were ob-
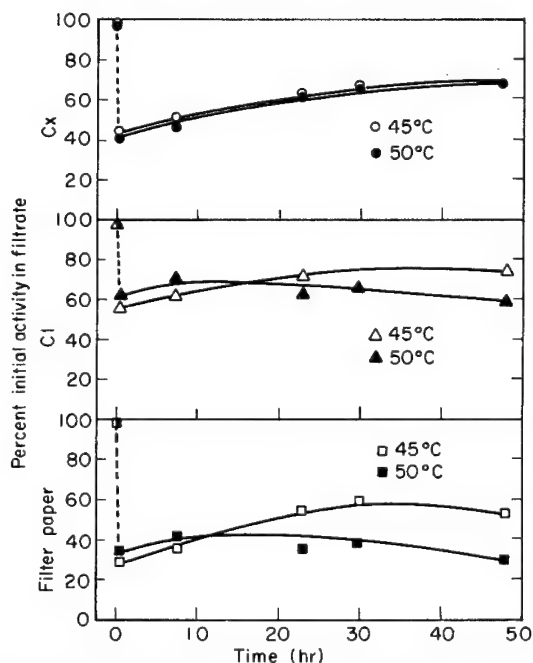
FIG. 2. Release of adsorbed enzyme during hydrolysis for initial FPA 3.5 and 5% solids.

tained in 48 hr for 2.5 FPA and 3.5 FPA, respectively. Comparison of these re-
sults with those of Table I suggests that the suspensions should be well-mixed for
maximum conversion.

As illustrated in Figure 2, enzyme is strongly adsorbed at the beginning and
then is gradually released into the solution as hydrolysis proceeds. The percent-
age of original activity remaining in the solution was evaluated for C_1, C_x, and
FPA activities by converting the respective activities after hydrolysis to enzyme
protein equivalent. The enzyme protein equivalent was determined from calibra-
tion curves prepared by dilution of fresh enzyme solution (see Fig. 4 for the case of
FPA). Operation at 45°C gives more potentially recoverable enzyme than at
50°C, presumably because of greater denaturization at the higher temperature.
However, the condition of the enzyme on the solids has not been conclusively de-
termined.

These results suggest that considerably more enzyme is released on the basis of
C_1 and C_x activity than on the basis of FPA. As a design basis for the process
proposed below, the amount of enzyme released to the product solution was as-
sumed to be 50% based on the value shown for FPA in Figure 2. Further study of
this problem appears desirable.

ENZYME ADSORPTION

From experiments with ball-milled paper, Wilke and Mitra [1] proposed in an
earlier process design that enzyme release to the sugar solution after hydrolysis
can be recovered by adsorption on the fresh feed to the process. Therefore, ad-
sorption measurements were made with the −20 mesh Wiley-milled paper to be
employed in the present design study. To measure adsorption various quantities
of ground newsprint were contacted with enzyme solution of 3.5 FPA, and the
amount of original activity in the solution was measured after contact of 40 min.
In washing experiments, solids from the previous experiment were separated by
centrifugation and resuspended in citrate buffer at pH 4.8. The amount of origi-
nal activity in the solution was measured after 40 min contact. Results shown in
Figure 3 indicate that C_x and C_1 are adsorbed to about the same extent. Based on
Figure 3, for subsequent design of adsorption systems, a distribution coefficient of
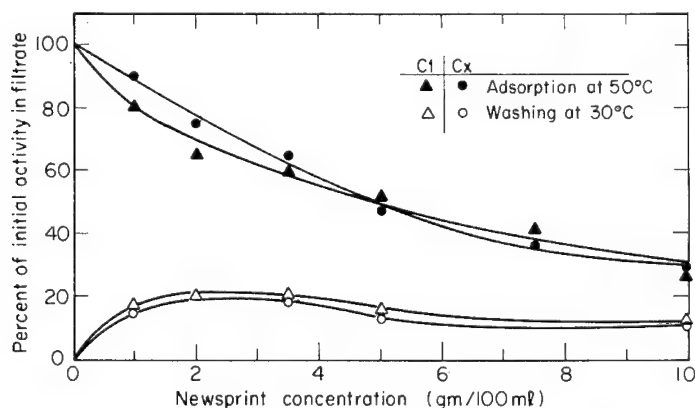
FIG. 3. Enzyme adsorption equilibria on newsprint at initial FPA of 3.5.

0.04 (FP units/ml)/(FP units/g solid) will be assumed (expressed as equivalent protein).

ENZYME DESORPTION FROM HYDROLYZED SOLIDS

The hydrolyzed solids described earlier in this paper were centrifuged from the original sugar solution and resuspended in buffer solution to determine the amount of enzyme released by desorption.   After centrifugation no activity could be detected in the supernatant, suggesting that the washing method for enzyme recovery proposed by Wilke and Mitrå would not be effective in this case.   This result is in sharp contrast to results obtained by Mitra and Wilke [6] for the distribution of fresh enzyme between buffer solution and paper which had been hydrolyzed to 82% conversion.   Further work is in progress to see if some desorption technique can be developed or if the adsorbed enzyme is irreversible denatured.   Meanwhile, it will be assumed that no enzyme recovery from the hydrolyzed solids is possible and that the quantity of enzyme retained on the solid will be consistent with the results described earlier.

ENZYME ACTIVITY IN RELATION TO SOLUBLE PROTEIN CONCENTRATION

A calibration curve for FPA versus enzyme protein was established as shown in Figure 4.   Enzyme protein was measured by modified Biuret method after precipitation with acetone.   Enzyme solution of FPA 2.75, corresponding to 0.85 mg/ml protein, was used as the starting material.   More concentrated solutions were prepared by precipitating the enzyme at room temperature with acetone (3:1 v/v) and redissolving the precipitate in appropriate volumes of citrate buffer of pH 4.8. More than 90% recovery of enzyme activity can be obtained by acetone precipitation, as is shown in the graph.
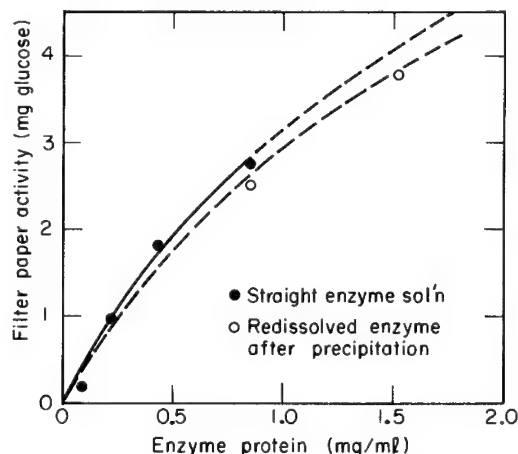
FIG. 4. Filter paper activity (FPA) vs. enzyme protein concentration.

A TENTATIVE HYDROLYSIS PROCESS

The foregoing laboratory results are employed as a basis for revision of the original Wilke-Mitra process [1]. In addition, a major modification in the enzyme-production operation involving use of cell recycle is introduced. This latter change is justified as follows.

Mitra and Wilke [6] specified a two-stage continuous fermentation operation for cellulase production. In the first stage, *Trichoderma viride* is grown rapidly on glucose to produce a relatively dense cell suspension. In the second stage cellulosic material is added in the absence of externally supplied glucose to induce the
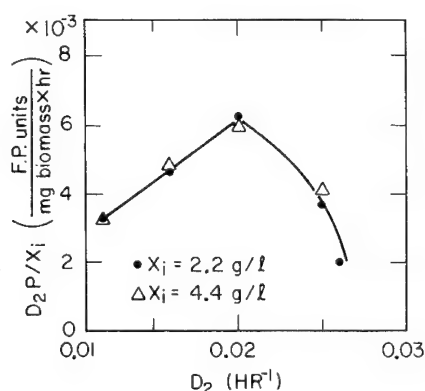
FIG. 5. Specific enzyme productivity per unit inlet biomass to the cellulose stage as a function of dilution rates. $X_1 \rightarrow$ inlet biomass to the cellulose stage, $P \rightarrow$ enzyme activity, $D_2 \rightarrow$ dilution rate. (After Mitra and Wilke [10].)
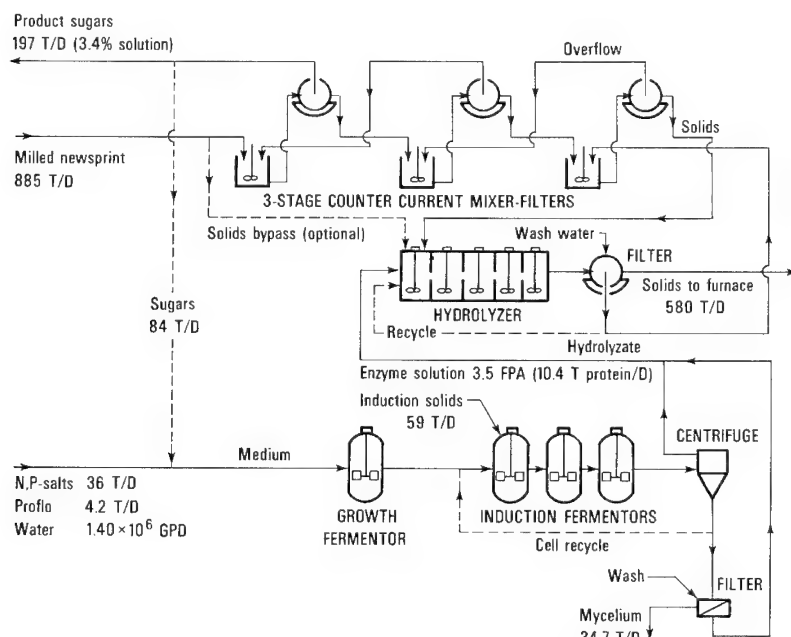
FIG. 6. Flow diagram for modified hydrolysis process.

TABLE II
Major Items of Equipment: Base Case

Item	Unit Specification	No. of units	Cost/unit, $ [a]
Enzyme Production		Total	$ 4,371,000
Cell growth fermentor (B_1)	Vol. 5.56×10^4 gals. agitator, stainless steel construction	10	75,000
Induction fermentor (B_2)	Vol. 5.2×10^5 gals. agitator, stainless steel construction	10	287,000
Agitator motor coupled with B_1	Variable speed drive unit rating 60 HP	10	5,000
Agitator motor coupled with B_2	Unit rating 300 HP	10	11,000
Air compressor coupled with B_1 and B_2	Centrifuger typ, 30 psig 17,000 CFM, 1650 HP	1	300,000
Heat exchanger for media sterilization	Shell and tube type, multiple exchange units for a total of 10,900 ft^2 of surface	1	53,870
Induction solid sterilizer	9' x 160' modified rotary kiln or dryer	1	31,200
Seed tank	Vol. 1500 gals. vessel, agitator and motor	1	14,000
Raw material mixing tank	Vol. 23,200 gals., agitator carbon steel construction, 60 HP motor	1	35,000
Centrifuge for cell recycle	De laval centrifuge 70 M^3/hr throughput	2	41,150
Mycelium filter	Pressure filter, effective area 175 ft^2	1	7,270
Hammermill for induction solids	Welded steel construction 3600 RPM motor, 3000 lb/hr	2	30,400
Screw conveyor for induction solids		1	3,500
Heat exchange tubing for temp. control in fermentors	A total of 400 ft^3 area, stainless steel	1	3,500
Pumps and drivers		12	2,500
Hydrolysis		Total	$ 3,214,400
Hydrolyzer (H)	Concrete digastor, agitator place below ground level. Vol. 1×10^6 gals.	7	395,000
Agitator motor coupled with H	Rating 500 HP	7	14,600
Solid filter	Vaccum drum filter plus accessory	1	227,200
Pumps and drivers	1400 GPM	4	2,500
Storage tank	1×10^6 gals., carbon steel	1	100,000
Heat exchange tubing	450 ft^2 area	2	2,500
Enzyme Recovery		Total	$ 775,140
Mixer	Agitator, carbon steel mixing vessel, vol. 7.4×10^4 gals.	3	21,700
Agitator coupled with above	Variable speed drive unit rating 50 HP	3	4,480
Filters for Adsorption	Horizontal belt filter plus accessory, 300 ft^2 effective area	3	227,200
Pumps and drivers	1400 GPM	6	2,500
Pretreatment		Total	$ 893,500
Hammermill	Welded steel construction 1800 RPM motor, air system with cyclone, capacity 2500-4000 lb/hr.	20	43,800
Screw conveyor	400 ft^3/hr, 10' x 30' 1.69 HP	5	3,500

[a] Costs are estimated for the 4th quarter 1974, Marshall Stevens Index = 431 [13].

enzyme. It was also shown that the enzyme productivity was directly proportional to the cell density in the induction stage, as is illustrated in Figure 5. On the basis of this observation, use of cell recycle around the induction stages is proposed to produce a higher cell density than would be possible otherwise. It is also assumed that the recycle cells will become fully adapted metabolically to enzyme induction following their synthesis on glucose in the growth stage.

The foregoing data and assumptions are incorporated in the processing scheme shown in Figure 6. Flow quantities are given on the diagram for a particular design specification which will be referred to as the "base case." Principal items of equipment corresponding to the flow sheet quantities are described in Table II. For simplicity, the facilities for milling, heat exchange, induction-solids sterilization and residual-solids combustion, have been omitted in the flow diagram, although they were designed and are included in the processing-cost analyses.

The primary plant feed consists of 885 tons/day of newsprint containing 6% moisture. By means of moderate shredding and hammermilling the feed is re-
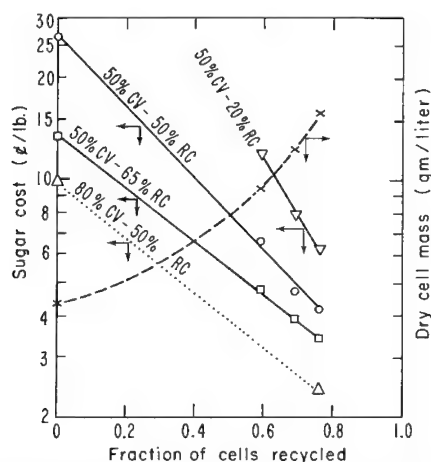
FIG. 7. Sugar cost as a function of the fraction of cells recycled over the introduction stages.

duced to approximately −20 mesh. The size reduction is not critical so long as the material will form aqueous suspensions which can be pumped, agitated and filtered. An additional 59 tons/day of feed material is diverted to the first enzyme induction fermentor after sterilization with steam. The product-sugar stream from the hydrolyzer is contacted countercurrently with feed solids for enzyme recovery. Each mixer filter stage consists of a mixing tank to provide 30 min contact time and a horizontal-belt vacuum filter to separate the solids from the liquid. A total enzyme recovery of 95% is predicted by theory based on the adsorption studies described earlier.

Hydrolysis is conducted over 40 hr at 45°C at a solid/liquid ratio of 1:20 w/w based on inputs to the hydrolyser. The latter consists of 5 agitated cylindrical concrete digestors of the type used for solid-waste treatment in sanitary engineering. Cellulose conversion of 50% is assumed, based on the data of Figure 2, at an overall enzyme strength equivalent to 3.5 FPA in the hydrolyzer. Provision is made for recycle of a portion of the product-sugar solution (plus enzyme) back to the hydrolysis vessel. A sugar concentration of 3.4% is obtained for the case

shown. A range of sugar levels is possible depending on the mode of operation and amount of sugar recycle employed.

Makeup enzyme is produced in a two-stage fermentation system as discussed above. Cell growth is obtained in the first stage at a dilution rate of 0.2 hr^{-1} employing a medium containing 1% product sugars plus minerals and Proflo as given in Table II. The induction system is operated at an overall dilution rate of 0.02 hr^{-1} using a 1.5% suspension of sterilized feed solids as inducer. Both stages employ agitated stainless steel vessels operated at 30°C with aeration rates of 0.15 and 0.015 v.v.m. in growth and induction stages, respectively. The growth-stage feed is sterilized in a heat-exchange system (not shown). The induction-section effluent is passed through a centrifuge from which a portion of the underflow is fed back to the first induction stage. Three to five induction stages in series are employed depending on the fraction of cells which is recycled. The flow quantities in Figure 7 correspond to a cell-concentrate recycle fraction of 0.11. Recycle fraction is defined as the ratio of the flow of cell concentrate from the centrifuge to the flow from the growth stage. The actual fraction of cells recycled is 0.59. For the case shown, the use of recycle increases the cell density in the induction system from 0.44% to 1.0% dry weight, and gives an increase of 125% over the cell concentration from the growth stage. The resultant increase in enzyme production is sufficient to provide an enzyme concentration of 3.5 FPA in the hydrolyzer without use of acetone precipitation. A portion of the centrifuge underflow is filtered and the cells discarded to maintain adequate cell viability. The centrifuge overflow will contain a small concentration of cells (0.029% in the case shown). Removal of these cells prior to hydrolysis is assumed to be unnecessary because *T. viride* will not grow at the hydrolysis temperature. However, further study of other possible problems of microbial contamination in the hydrolysis system is needed.

Spent solids from the hydrolyzer following filtration are fed to a furnace and steam-power plant to provide process steam and electricity for the process. A substantial excess of energy is available in the spent solids, sufficient to operate an alcohol fermentation plant, for example, and to produce some additional by-product power. No credit is assumed for this excess energy in the processing-cost analysis described below, pending a more detailed study of the combustion operation.

Base-Case Cost Estimation

For the process described above, a preliminary cost estimate was made for the required capital investment and cost per pound of sugars produced in aqueous solution.

The general cost estimation procedure was that recommended by Peters and Timmerhaus [11] and by Holland and co-workers [12].

The fixed-capital cost is estimated as a multiple of purchased cost of the principal items of equipment. In the present case a multiplier of 3.1 was used, except in the case of the concrete digestors for which the multiple was reduced to 1.68 because the unit cost already included engineering construction and contractor's fees. Estimated costs of the principal equipment items are listed in Table II. The total manufacturing cost is broken down into investment-related costs, labor-related costs, utilities costs and raw-material costs. Multipliers and unit costs for the

TABLE III
Investment-Related Cost Factors (Annual Cost = Factor × Fixed Capital)

ITEM	COST FACTOR
DEPRECIATION	0.10
INTEREST	0.06
MAINTENANCE	0.06
INSURANCE	0.01
PLANT SUPPLIES	0.009
TAXES	0.00

TABLE IV
Labor-Related Cost Factors (Cost = Factor × Labor Cost)

ITEM	COST FACTOR
DIRECT LABOR COST	1.00
SUPERVISION	0.15
PAYROLL OVERHEAD	0.15
LABORATORY	0.15
PLANT OVERHEAD	0.50

TABLE V
Utilities Costs: Base Case

	UNIT	UNIT COST	UNITS/HR.
POWER	KWH	0.75¢	8338
STEAM	1000 LB.	32.5¢	36
WATER	1000 GAL.	40.0¢	83

TABLE VI
Medium Raw Materials: Base Case

COMPONENT	GM/LIT.	$/TON	TONS/DAY
AMMONIUM SULFATE	1.4	90	11.68
POTASIUM PHOSPHATE	2.0	120	16 70
CALCIUM CHLORIDE	0.3	33	2.50
MAGNESIUM SULFATE	0.3	110	2.50
UREA	0.3	160	2.50
PROTEIN NUTRIENT	0.5	300	4.17

component cost items are listed in Tables III–VI. A base-labor rate of $4.00 per hour is assumed. Taxes are omitted on the assumption that the installation would be part of a municipal waste-processing complex. No charge or credit has been assigned to the newsprint. Costs of process steam and power were estimated assuming that they could be generated on the plant site using spent solids as fuel. Capital costs for steam-power facilities are not included in the fixed capital costs on the assumption that the specified unit costs for steam and electricity include both investment and labor charges. An on-stream efficiency of 90% is assumed, corresponding to 330 days operation per calendar year.

The resulting fixed-capital cost, total manufacturing costs and costs per unit of product are listed in Table VII for each of the major processing sections: (1) hydrolysis, (2) pretreatment, (3) enzyme recovery, and (4) enzyme makeup. For this base case a fixed-capital cost of $24,448,000 and a sugar cost of 6.56¢ per

TABLE VII
Process-Cost Analysis: Base Case (Cell Recycle Fraction = 0.59)

	HYDROLYSIS	PRETREATMENT	ENZYME RECOVERY	ENZYME MAKE-UP	TOTAL
FIXED CAPITAL COST, $	6,020,350	2,734,110	2,319,300	13,375,000	24,448,760
Annual investment related costs, $	1,438,900	653,450	554,310	3,196,600	5,843,260
Annual labor related costs, $	122,990	61,495	122,990	122,990	430,465
Annual Utilities costs, $	189,090	79,860	39,270	287,430	605,650
Annual raw materials costs, $	-	-	-	1,656,800	1,656,800
ANNUAL MANUFACTURING COSTS, $	1,750,980	794,800	716,580	5,263,820	8,526,180
DAILY MANUFACTURING COST, $	5,306	2,408	2,171	15,950	25,837
SUGARS COST, ¢/lb.	1.35	0.61	0.554	4.07	6.56

pound is obtained. Enzyme makeup is the major cost factor, comprising over 60% of the total. Alternative design specifications will now be considered.

Effects of Alternative Process Design Bases

Cell Recycle

Because the use of cell recycle over the induction stages is a major factor in achieving a low enzyme cost, several additional design cases were evaluated at other recycle fractions, including one case with no recycle. In the latter case, it

TABLE VIII
Process-Cost Analysis (Cell Recycle Fraction = 0.76)

	HYDROLYSIS	PRETREATMENT	ENZYME RECOVERY	ENZYME MAKE-UP	TOTAL
FIXED CAPITAL COST, $	6,020,350	2,734,110	2,319,300	7,918,000	18,991,760
Annual investment related costs, $	1,438,900	653,450	554,310	1,892,390	4,539,050
Annual labor related costs, $	122,990	61,495	122,990	122,990	430,465
Annual Utilities costs, $	189,090	79,860	39,270	170,158	478,378
Annual raw materials costs, $	-	-	-	90,826	980,826
ANNUAL MANUFACTURING COST, $	1,751,000	794,800	716,500	3,166,360	6,428,180
DAILY MANUFACTURING COST, $	5,306	2,403	2,171	9,595	19,479
SUGARS COST, ¢/lb.	1.14	0.52	0.47	2.07	4.2

was necessary to concentrate the enzyme solution from the growth state to 3.5 FPA by precipitating the protein with acetone and redissolving it in the hydrolyzer liquid. The design and costs for the acetone system were estimated in the manner described previously by Wilke and Mitra [1] and will not be described in detail here since this method of operation is not attractive economically.

The top line of Figure 7 depicts approximately the variation of sugar cost with the fraction of cells recycled. A probable most favorable case is that for a recycle fraction of 0.76, which is about the maximum which seems feasible. As shown by the dotted line, the cell density increases from 4.4 g (dry weight)/l. to 17 g/l. over the recycle range. Detailed investment and operating costs for this case are given in Table VIII. In comparison with the base design case the fixed-capital cost is reduced to approximately $19,000,000 and the sugar cost becomes 4.2¢ per lb.

Enzyme Recovery

In the design cases considered thus far, it has been assumed that 50% of the enzyme in the hydrolyzers is discharged in the hydrolysis solution and is recoverable in the adsorption section. Further study of this problem seem desirable in view of the difference in release of C_1 and C_x activities (shown in Fig. 2) compared to that of filter paper activity, and since the experimental data are rather limited in scope. Therefore, additional cost estimates were prepared for enzyme recoveries of 65% and 20%, on the assumption that the recovery ultimately obtainable in practice will fall within this range. The effects of these assumptions on the sugar production cost are illustrated by the corresponding lines on Figure 7. It is apparent that efforts to improve the degree of enzyme recovery could be very worthwhile.

Percentage Cellulose Conversion

The dotted line of Figure 7 shows the substantial cost improvement which would be possible if somehow the level of cellulose hydrolysis could be increased from 50% to 80% without increase of the processing costs. Table IX shows the pretreatment (chemical or milling) cost which would be allowable to achieve various levels of conversion and corresponding sugar costs. For example, it would be feasible to pay $19 per ton for pretreatment to increase the conversion level to 80% and match the cost for the design case with 50% conversion and $2.70 per ton for milling. This type of consideration could be particularly important if a charge must be made for the raw material.

TABLE IX
Allowable Pretreatment Cost to Obtain Higher Conversion

CELL RECYCLE	% CONVERSION	¢/LB. SUGAR COST	$/TON ALLOWABLE PRETREATMENT
0.76	50	4.2	2.7
0.76	70	3.5	8.0
0.76	80	2.4	2.7
0.76	80	3.6	13.0
0.76	80	4.2	19.0

Effects of Taxes, Interest, and Raw-Material Cost

Table X shows the incremental cost per pound of sugar at a cell recycle of 0.76 resulting from variations in the costs of taxes, interest, and raw materials. The base case assumptions of zero taxes and 6% interest corresponding to a municipal operation do not appear particularly serious, since increasing these variables to values typical of the present private economy will not increase the product costs very much. A more serious factor is the potential cost of the raw material. A zero raw-material cost may be reasonable for a municipal waste-disposal operation in which the material has to be collected and disposed of whether or not a hydrolysis plant is used. Because of the variability of waste paper costs in the open market no attempt will be made in this paper to evaluate the raw-material question in further detail.

TABLE X
Effect of Variables on Product Cost (Cell Recycle Fraction = 0.76)

VARIABLE	INCREASE OF VARIABLE	¢/LB INCREASE OF SUGAR COST
COST OF PAPER	$20/TON	3.85
TAXES	0 TO 3%	0.36
INTEREST	6% TO 12%	0.75

CONCLUSION

The foregoing analyses suggest that it may be economically feasible to produce sugars from waste newsprint by enzymatic hydrolysis, and that a similar conclusion may be extended to various other cellulosic materials pending more specific studies. However, it should be recognized that many uncertainties exist in the proposed processing methods and cost estimates. Research and development work, including pilot-plant studies, should be continued to improve the technology and provide a more firm basis for design of large-scale processing plants.

More effective utilization of other components of cellulosic materials including lignin and hemicellulose should also be considered for their potential economic benefit.

REFERENCES

[1] C. R. Wilke and G. Mitra, in *Cellulose as a Chemical and Energy Resource (Biotechnology Bioengineering Symp.* No. 57, C. R. Wilke, ed, Wiley-Interscience, New York, 1975, P. 253.

[2] C. R. Wilke and R. D. Yang, SITRA Symposium on Enzymatic Hydrolysis of Cellulose, Hämeenlinna, Finland, March 1975.

[3] M. Mandels, J. Weber, and R. Parizek, *Appl. Microbiol., 21,* 152 (1971).

[4] M. Mandels and J. Weber, *Advan. Chem. Ser., 95,* 391 (1969).

[5] J. B. Summer and G. F. Somers, *Laboratory Experiments in Biological Chemistry,* Academic Press, New York, 1949.

[6] G. Mitra and C. R. Wilke, *Enzymatic Utilization of Waste Cellulosics,* Lawrence Berkeley Lab. Report 2334 (rev.), April 1975.

[7] T. K. Ghose and J. A. Kostick, *Advan. Chem. Ser., 95,* 415 (1969).

[8] B. Rubik, private communication, Lawrence Berkeley Lab., October 1974.

[9] M. Mandels, L. Hontz, and J. Nystrom, *Biotechnol. Bioeng., 16,* 1471 (1974).

[10] G. Mitra and C. R. Wilke, *Biotechnol. Bioeng., 17,* 1 (1975).

[11] J. S. Peters and K. D. Timmerhaus, *Plant Design and Economics for Chemical Engineers,* McGraw-Hill Book Co., New York, 1968.

[12] F. A. Holland, F. A. Watson, and J. K. Wilkinson, *Introduction to Process Economics,* John Wiley & Sons, Ltd., London, 1974.

[13] "Marshall and Stevens Equipment Cost Index—Process Industries Average," *Chem. Eng., 82*(3), 120 (1975).

PROTEINS FROM WASTE CELLULOSE

CLAYTON D. CALLIHAN, GEORGE H. IRWIN, JAMES E. CLEMMER, and OLIVER W. HARGROVE

Chemical Engineering Department,
Louisiana State University, Baton Rouge, Louisiana 70803

SYNOPSIS

The shortage of oil and natural gas has already been reflected in shortages and spiraling prices for all products based on hydrocarbons. This paper presents data to show that in a great many areas this organic base can easily be changed from hydrocarbons, a nonrenewable resource, to cellulose which is perpetually replaced by photosynthesis. One example of this changeover is demonstrated here for the production of food.

None of the many research projects we work on could ever have any real meaning unless they lead to commercialization and mass production, because only in this way can the research results hope to improve the lives of humans. A researcher has a duty, not only to attract research money, but also to venture capital for commercialization. In order to get businessmen to invest this relatively high-risk capital, certain technological advantages must be available to them. If you feel that we are leaving out a few of the technical details in our discussion today, you will be entirely correct. We feel it is our duty to protect venture capital.

The shortage of oil and natural gas will soon be reflected in shortages and spiraling prices for all of those products that are now based on hydrocarbons. Ammonia, for example, is produced from natural gas, and its price is soaring. Yet ammonia is required as fertilizer to produce food. Since food is already scarce and expensive, another way must be found to produce food or to make fertilizer. The cost of energy to power tractors, to cultivate, to harvest, to can, to distribute, etc., is increasing dramatically.

In addition to food supplies, almost our entire field of synthetic polymers such as plastics, fibers, elastomers, films, clothing, etc., are entirely dependent on oil and natural gas. These hydrocarbons are disappearing at an alarming rate, not only because our own consumption is tremendous, but also because the developing nations are increasing their consumption. The net result is an exponential increase in the use of hydrocarbons with an ever-dwindling supply. Wars can and are being fought to obtain production rights on those relatively small deposits of hydrocarbons still remaining.
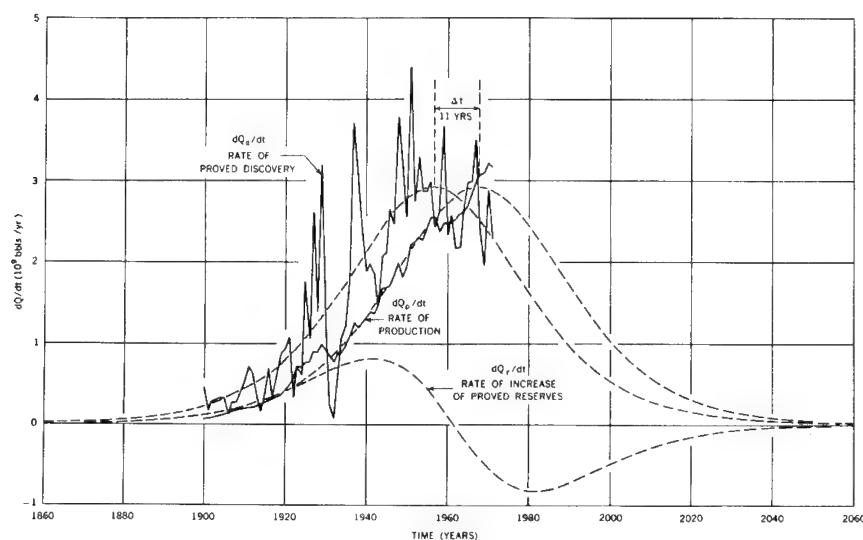
FIG. 1. Annual production and proved discoveries of crude oil in the conterminous United States from 1900 to 1971 superposed on the theoretical curves (dashed). (From U.S. Energy Resources, a Review as of 1972, Part I, by M. King Hubbert.)

It is tremendously important for the peoples in the world to recognize the transitory existence of this nonrenewable resource. It is no longer a question of whether the oil and gas will all be consumed; the only question that remains is when. One of the most realistic approaches to this question has been taken by Hubbert (U.S. Department of the Interior, Reston, VA 22092), Chairman of the U.S. Energy Resources Study Group, who has collected data to show that oil reserves are dropping rapidly while consumption is increasing exponentially as shown in Figure 1. The
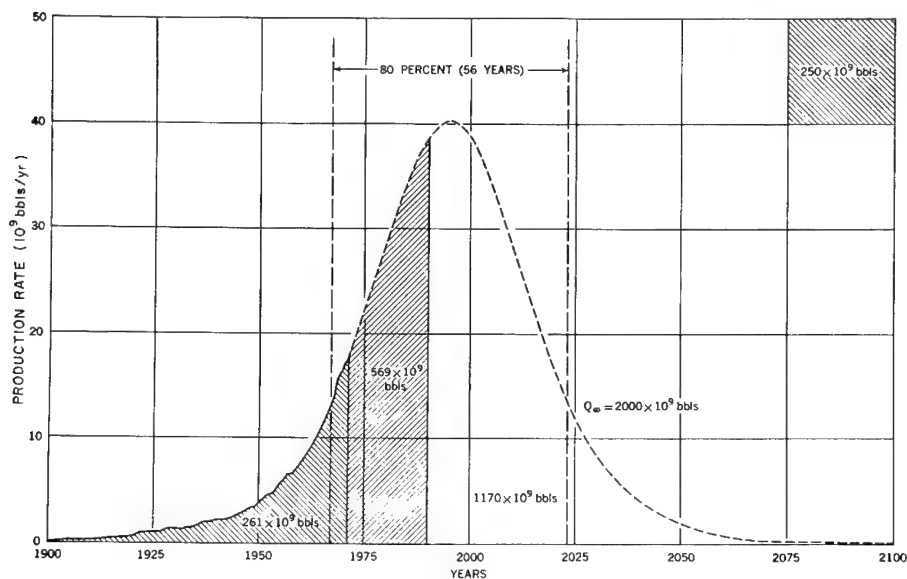
FIG. 2. Estimate as of 1972 of complete cycle of world crude-oil production. (From U.S. Energy Resources, a Review as of 1972, Part I, by M. King Hubbert.)

conclusion this group reached was that before the turn of the century, oil and gas production will be decreasing at the same rate that production and consumption have been increasing over the last 50 years, as summarized in Figure 2. Simply stated, hydrocarbons will soon become very scarce and then disappear. Figure 3 taken from Hubbert's report put the consumption of a nonrenewable resource in its proper time perspective.

If the peoples in the world will only recognize the dangers inherent in this situation, they will immediately change from a hydrocarbon-based economy to a cellulose-based economy. Cellulose is a renewable resource and millions of tons are produced daily by the process of photosynthesis. Since the other product of photosynthesis is oxygen, cultivation of cellulose should appeal greatly to those who worry about the high level of carbon dioxide in the air.

To wait until all the oil and gas have been exhausted before changing to a cellulose-based economy would be nothing short of disastrous. The changeover should start immediately, if for no other reason than to prevent the flow of the world's money supply to those few countries that still have excess oil and gas.

Cellulose is a remarkable material which we often seem to ignore when it could mean so much to us. It comes in nature associated with lignin and carbohydrates of all kinds. All of the essential building blocks are present in trees and plants to produce practically any chemical we wish. Lignin contains a benzene ring as well as alkyl substituents. As a matter of fact, pyrolysis and cracking of these by-products of cellulose production should not be difficult, and a major research thrust should be made to prove it. Living plants are by far the best and most efficient solar-energy collectors known to man. Certainly no one can deny that they are the cheapest. One of the nice things about cellulose is that it is already a polymer. It needs no polymerization step to make it into fibers or plastics or whatever synthetic material is needed.

Actually, the process for making cellulose into useful synthetics is quite easy. It requires only a simple substitution of the hydroxy groups along its chain to change it into water-soluble thickeners, into plastics, to fibers, to films, to lacquers, or whatever. Unfortunately, although many of these processes were developed years ago, most people have turned their attention to polyethylene, polypropylene, polybutadiene, etc., and have almost completely forgotten about this one material that they can always count on. At Louisiana State University, we have not forgotten about cellulose polymers and have been busily carrying out research on
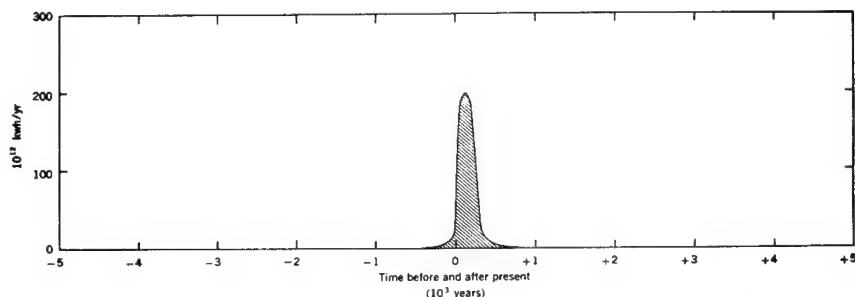
FIG. 3. The epoch of fossil-fuel exploitation as seen on a time scale of human history from 5,000 years ago to 5,000 in the future. (From U.S. Energy Resources, a Review as of 1972, Part I, by M. King Hubbert.)

NATIVE CELLULOSE

$$C_1 \quad \text{(Alkali Treatment)}$$
$$\downarrow$$

LINEAR CELLULOSE

$$C_x$$
$$\downarrow$$

CELLOBIOSE

$$\beta - \text{Glucosidase}$$
$$\downarrow$$

GLUCOSE

Metabolic Pathway
$$\downarrow$$

CELL MASS

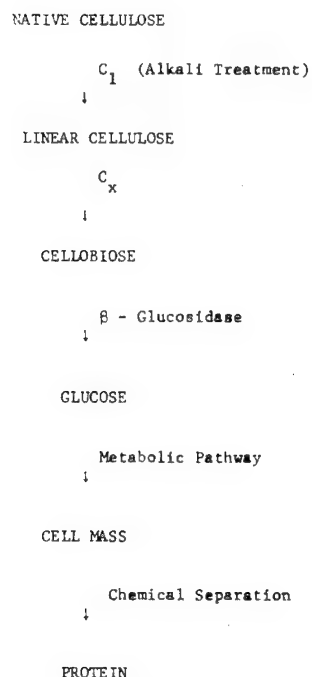Chemical Separation
$$\downarrow$$

PROTEIN

FIG. 4.

many cellulose derivatives, trying to make their production steps more economical, as well as preparing new derivatives for the future.

Of the many wonderful things about cellulose, perhaps the very best is that it is also a food. The simple anhydroglucose units that make up the cellulose backbone can be set free by cutting the oxygen bridge that binds them into the chain. Once released, they are glucose molecules, a very good source of energy for all of us. Glucose is released by a hydrolysis step either chemically or enzymatically. In World War II, when the Germans were faced with almost identical shortages as those we face today, they hydrolyzed cellulose with acid to produce glucose and then grew yeast on it. The yeast was fed to the people as a source of protein. Acid hydrolysis is rather expensive and seems to be largely confined to the amorphous regions of the cellulose, leaving the inaccessible crystalline regions.

At LSU, we have developed a process for the enzymatic hydrolysis of cellulose followed by consumption of the glucose with a bacterium, *Cellulomonas flavigena*. In order to carry out an enzymatic hydrolysis of cellulose, the cellulase enzymes must be able to penetrate to and attack the cellulose molecules. Most cellulase enzyme systems have a C_1 enzyme as shown in Figure 4. Its function appears to be that of swelling or disrupting the strong van der Waals forces that hold the molecules together. Our bacteria do not have this capability, so we must carry out the swelling step by a pretreatment. In our process, this is normally done with a very dilute solution of caustic or sodium hydroxide at elevated temperatures.

During the alkali treatment, some of the caustic is consumed to neutralize various acid groups formed by the high temperature treatment as shown in Figure 5. After the alkali treatment, the cellulose is thoroughly washed to remove any solubilized carbohydrate, unconsumed caustic, depolymerized lignin, etc. The remov-
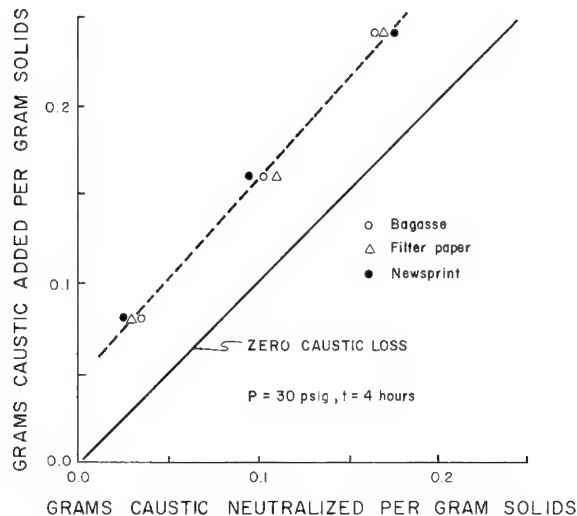
FIG. 5. Loss of caustic during treatment.

al of soluble sugar is necessary for two reasons. One is that the cellulase enzymes are inducible, so that the presence of soluble carbohydrates suppresses cellulase activity. The second reason is sterility. Any invading organism can live on glucose but very few can live on pure cellulose.

For native cellulosics such as bagasse, slightly over half of the initial feed material is lost to fermentation during treatment and washing. Of course, these materials can be recovered for manufacture into chemicals, fuel, etc. Material balances are shown in Figure 6. A similar loss must be experienced for any process where microorganisms convert cellulose into biomass, because the lignin and other
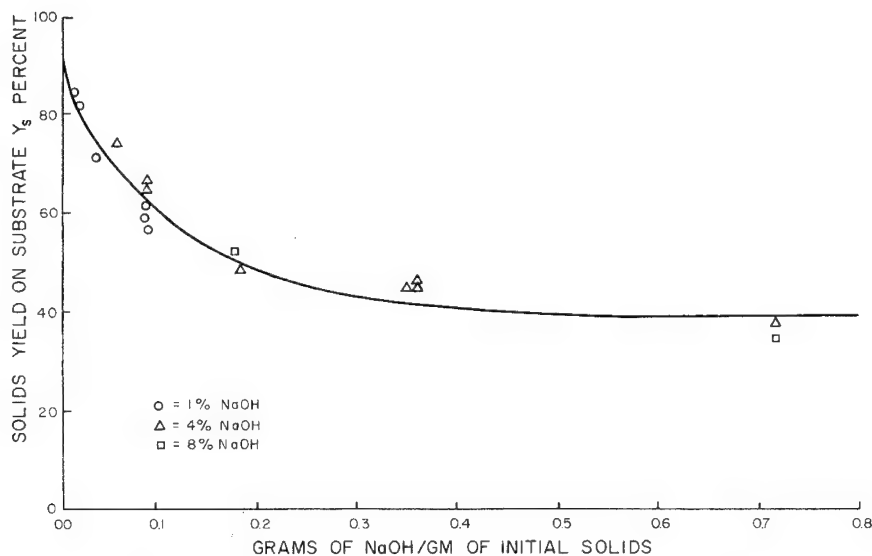
FIG. 6. Substrate remaining after NaOH treatment (4 hr at 130°C).
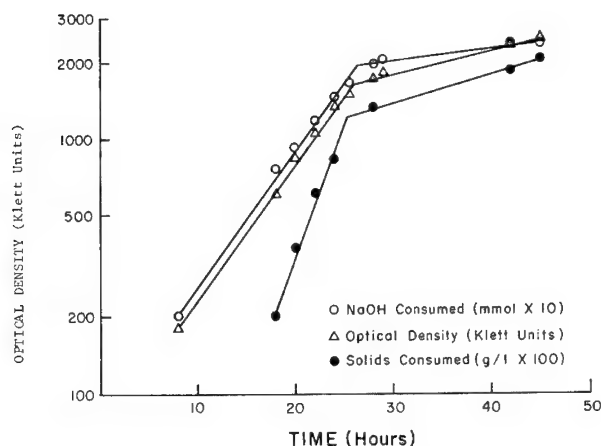
FIG. 7. Typical microbial growth curve (*Cellulomonas* on alkali-treated bagasse).

components in native cellulose are usually not consumed by organisms at a sufficient rate to produce reasonable amounts of biomass.

After washing, the cellulose is introduced into a fermenter, where nutrients and fertilizers are added. In typical fermentations on glucose or soluble carbohydrates, sterilization must be performed on the nutrients and trace minerals separately to prevent caramelization. When using native cellulose as a substrate, there appears to be no deleterious effects of sterilization on the premixed system. In the case of sugar cane bagasse, however, a dual sterilization appears to be necessary because of the presence of spore formers in the native cellulose. The spores are usually allowed to flower after the first sterilization, and these are subsequently killed while still in the vegetative state by a second sterilization.

After sterilization is complete, the reactor mass is cooled to 33°C, and the pH is adjusted to 6.5 to 6.8. A 10% inoculum is then added. Filtered air is initially introduced at a slow flow rate, and the turbine speed is also set relatively slow for the first stage. If the inoculum is properly prepared, there is no lag phase such as that normally experienced with batch fermentation on a soluble substrate.

Early in our research, we experienced a great deal of difficulty in monitoring cell growth. It is easy to see that turbidity measurements would have little meaning if the sample contains suspended particles of unreacted cellulose. The cellulase enzymes of Cellulomonas flavigena are not extracellular but are cell-wall-bound. Therefore, in order to perform the hydrolysis step, the enzymes must fas-

TABLE I

Breakpoint Analysis of Alkali-Treated Bagasse

Experiment Number	Alkali Pretreatment T(°C)	Alkali Pretreatment t(hrs)	Alkali Pretreatment L/S	Alkali Pretreatment N	L/S	S_o [a] (g/l)	$(C)_{bp}$ [b] (g/l)	t_{md} [b]	$(S)_{bp}$ (g/l)	$(S/C)_{bp}$
7-3-20	121	1	20	.1	.67	16.6	3.32	4.0	5.5	1.66
7-3-32	121	2	3	.12	.70	13.1	2.71	6.0	4.4	1.62
7-4-32	121	2	3	.12	.70	23.1	6.47	5.5	12.1	1.87
7-5-32	121	2	3	.12	.70	34.6	8.0	7.0	14.8	1.85
7-3-33	99	2	4	.12	.67	24.5	7.06	3.5	13.9	1.97

[a] S_o = Initial substrate loading.
[b] Cell concentration and mass-doubling times are based on NaOH consumption.

ten to the relatively large cellulose particles which in turn binds the microorganisms to the cellulose. If attempts are made to remove the cellulose before turbidity measurements, a large number of cells are removed with the cellulose.

Fortunately for us, as the fermentation proceeds, the microorganisms remove nitrogen from the fertilizer, leaving behind an anion that must be neutralized with base to keep the pH constant. The amount of base consumed is related to the biomass production by a yield factor. Figure 7 shows 3 different monitors of cell growth on alkali-treated bagasse. Turbidity measurements and caustic consumption follow parallel paths as long as the yield remains constant. When the yield starts to decrease, turbidity falls off, while caustic consumption continues on its exponential path.
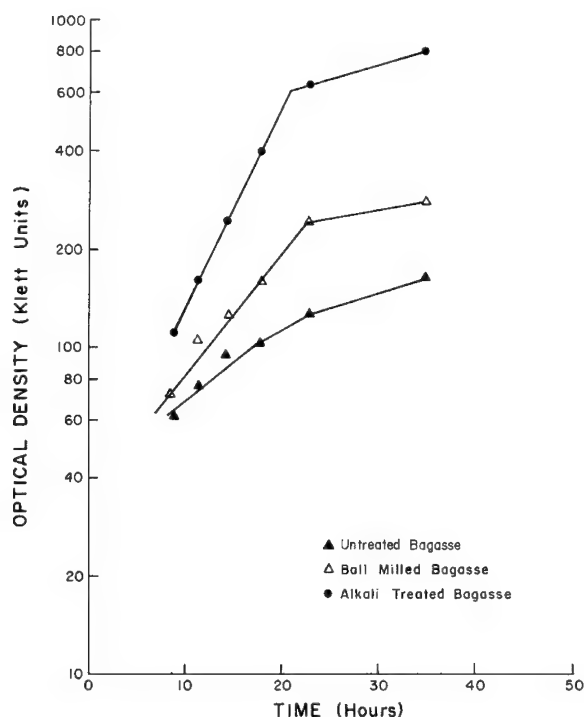
FIG. 8. Physical vs. chemical pretreatment of sugar cane bagasse.

The ideal conditions for a commercial fermentation process would be for the organism to grow at a fast rate while consuming a majority of the substrate at a reasonable yield. It is necessary, therefore, to have a large amount of growth occur in the logarithmic phase.

Under batch operation, in our system, this is a function of the pretreatment conditions. This extent of growth was determined by the ratio of the substrate concentration to cell concentration at the breakpoint in the growth curve $(S/C)_{bp}$. It was hypothesized that this ratio should be constant for a particular treatment of a substrate and not influenced by initial substrate loading or level of inoculum used. The change in growth at the breakpoint must be due to a lack of available sites to which the cells can attach. The growth rate prior to the breakpoint was measured as the mass-doubling time (t_{md}). These parameters are listed in Table I for some

seven-liter fermentations. The parameters were calculated using caustic consumption as a measure of cell concentration and mass-doubling time.

In general, it would be desirable to have the substrate to cell concentration $(S/C)_{bp}$ as low as possible because this indicates that a large extent of the cellulose consumption occurs in the exponential phase of growth. It might be expected then that if a given cellulose pretreatment caused rapid cell growth, this could imply that a large portion of the growth would occur at a rapid rate. This appears, however, not always to be the case. For example, the severely alkali-treated bagasse showed a slow rate of growth, but this rate was maintained for an extended period of time before the rate changed. This may mean that the strong alkali treatment leaves some inhibitory substance in the substrate that prevents rapid attachment by the enzymes, but that essentially all of the cellulose fibers have the same structure or are more uniform than those obtained by other treatments.

It is emphasized that a combination of doubling time and substrate to cell ratio must be considered when analyzing the value of the various treatments. However, while this parameter is felt to be mainly a function of the substrate and its treatment, there are many conditions which could influence the growth rate. Not enough is known at this time about enzyme activity and cell physiology to hypothesize what actually controls the cell growth rate. The substrate is only one of many variables which could affect it.

Many other types of pretreatment have been used on the bagasse to see if they might improve the growth rates. For example, some untreated bagasse was ball-milled for 24 hr and then used as a substrate to compare it to the regular alkali-treated bagasse. These results are shown in Figure 8 and indicate that ball-milling improved the growth rates only very slightly over untreated material.

After fermentation is over, the cell suspension is sent to a settling tank where the unreacted cellulose is settled out before the supernatant is sent to a centrifuge for cell harvest. The wet cell paste is then subjected to a high-temperature heat shock to kill the organisms before drying.

The product is a brownish flour that contains about 55% protein with a good amino-acid distribution. The lysine content is slightly higher than that of soybean protein (7.87 versus 6.6%) while the methionine content is considerably higher (2.16 versus 1.10%). Furthermore, the total protein content of soybean flour is only about 43%.

In terms of projected production costs, it appears that our process will be competitive on a per pound of protein basis with soybean flour. The Bechtel Corporation and the LSU Foundation have formed a joint venture for the purpose of bringing the process described in this paper to a point from which it can be commercialized.

CONVERSION OF CELLULOSIC WASTE INTO PROTEIN

MATS EK and KARL-ERIK ERIKSSON

Swedish Forest Products Research Laboratory,
Chemistry Department Box 5604, S-114 86 Stockholm, Sweden

For a long time we have been studying the mechanisms involved in the enzymic degradation of cellulose by rot fungi. With the knowledge we have gained here and the severe shortage of protein in the world as a background, we decided to work on the conversion of lignocellulosic waste materials into protein-rich microorganisms that can be used as fodder.

I should first like to give a brief summary of some of our basic research in the field. The fungus we used in our laboratory was of the white-rot type, namely, *Sporotrichum pulverulentum.* The fungus degrades cellulose, hemicellulose and lignin. Our strain was isolated from chip piles in Sweden, where it caused severe degradation of cellulose.

In the studies of the mechanisms of the enzymic degradation of cellulose, the fungus was cultivated in shake flasks with cellulose powder as the sole carbon source. Nutrient salts were added to support adequate growth, and the flasks were inoculated with a spore suspension after sterilization. After 5–6 days the fungus had solubilized all the cellulose, and the culture solution was concentrated in order to allow separation and purification of the enzymes. From this culture solution, five endo-1,4-β-glucanases and one exo-1,4-β-glucanase have been isolated [1,2]. The endo-1,4-β-glucanases hydrolyze β-1,4-glucosidic bonds randomly along the cellulose chain, while the exo-1,4-β-glucanase splits off cellobiose or glucose from the nonreducing end. We have demonstrated that the endo- and exoglucanases act in a synergistic manner; i.e., in the presence of both types of enzyme the cellulose is degraded to an extent which exceeds the total degradation by the two different types of enzyme separately.

In addition to the hydrolytic type of enzymes described above, we recently isolated a hitherto unknown enzyme which causes oxidation of the cellulose [3]. It seemed to oxidize the hydroxyl group in the 6-position in the glucose unit to a carboxylic group. This newly found enzyme is obviously important for cellulose degradation, since the degradation is approximately doubled when it is present in addition to the hydrolyzing enzymes (Table I).

Yet another enzyme of importance in both cellulose and lignin degradation was recently discovered in our laboratory [4–6]. It is called cellobiose:quinone oxido-

197

TABLE I

Degradation of Cotton Cellulose by Enzymes from *Sporotrichum pulverulentum*

Enzyme preparation	Cellulose degradation weight loss %
Concentrated culture solution	52.1 (oxygen atmosphere)
Concentrated culture solution	21.5 (nitrogen atmosphere)
Mixture of endo- and exo-glucanases	20.0
Endo-1,4-β-glucanases	0.0
Exo-1,4-β-glucanase	0.0

reductase and its mode of action is apparent in Figure 1, where it can be seen that it reduces quinones or phenoxy radicals in the presence of cellobiose. The cellobiose is converted to cellobiono-δ-lactone and subsequently to cellobionic acid by a lactonase.

Two processes are in technical use for production of protein from spent sulfite liquor, which consists partly of cellulosic waste. One of these processes has been used for a considerable time and produces fodder yeast by cultivation of *Candida utilis*. In this process the yeast grows on monosaccharides—both hexoses and pentoses—in the spent liquor. A number of factories of this type are in operation all over the world. Recently, a plant started in Finland with an annual yeast production of 10,000 tons.

Simultaneously, also in Finland, the recently developed Pekilo process has come into technical use for the fermentation of spent sulfite liquor. This process is similar to the *Candida utilis* process, since it also utilizes mainly the monosaccharides, although disaccharides can also be used at a lower rate. The greatest advantage of the Pekilo process is that the mycelial fungus used, *Paecilomyces varioti,* can easily be filtered off and further dewatered. The yeast has to be separated from the medium by centrifugation which is much more expensive. The product is also
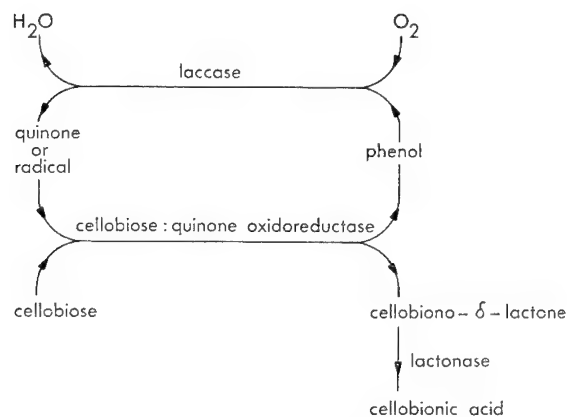
FIG. 1. Proposed mechanism of action for cellobiose:quinone oxidoreductase.

TABLE II

The Protein Content in *Sporotrichum pulverulentum* Grown on Different Carbon Sources.
Nitrogen Source: $NH_4H_2PO_4$

Carbon source	% protein in the mycelium
Glucose	42.3
Cellobiose	40.2
Walseth-cellulose	32.0
MoDo-silk	29.7
Cotton DP 500	22.8
Cotton DP 2000	21.7
Waste mechanical fibres	13.8
Powdered cellulose	6.0

reported to have a higher protein content and higher nutritional value than fodder yeast. On the other hand, the Pekilo process seems to be less resistant to infections, and this makes the fermentor more expensive.

Both the Candida and the Pekilo processes are mainly restricted to monosaccharides and acetic acid as substrates in technical use. Neither of the processes can use water-soluble oligomers and certainly not insoluble polysaccharides. These and other solid substrates have to be hydrolyzed before the fermentation can start. The great amount of carbohydrate waste of this kind and the shortage of protein have initiated much research all over the world. Fermentation after acidic hydrolysis of sawdust and other wood materials is in technical use at least in Eastern Europe, but it is normally considered uneconomical by western economic standards. Enzymatic hydrolysis is under development mainly in the U.S., and promising results have been obtained.

The aim of our fermentation research is to develop a process based on solid lignocellulosic waste in which the hydrolysis and the protein production are carried out simultaneously. A white-rot fungus is used as the active organism. With this aim we first developed a method that made it possible to grow the fungus on one side of a membrane with the carbon source, the lignocellulosic fibres, on the other side [7]. In this way it was easy to determine growth and fiber breakdown by weighing the fungal mycelium and the remaining fiber after drying. The membrane was a nylon cloth of pore size 28 μm. It is permeable to the extracellular enzymes produced by the fungus and to the water-soluble degradation products from the fibers but impermeable to the fibers and to the fungus. Growth was not affected by the membrane.

The experiments were carried out in shake flasks without continuous pH-control. The concentration of protein in the mycelium of *Sporotrichum pulverulentum* grown on different carbon sources with different DP's and different crystallinities could easily be compared in this way [7]. From Table II it is evident that a highly crystalline or a lignin-containing substrate is more difficult to utilize and gives a product with a lower protein content. The influence of DP is not very pronounced. The two types of cotton differ only in DP. A comparison between

TABLE III
The Composition of the Medium

	GRAMS PER LITRE
KH_2PO_4	0.6
K_2HPO_4	0.4
$MgSO_4\ 7\,H_2O$	0.5
$CaCl_2\ 2\,H_2O$	$74 \cdot 10^{-3}$
Ferricitrate	$12 \cdot 10^{-3}$
$ZnSO_4\ 7\,H_2O$	$6.6 \cdot 10^{-3}$
$MnSO_4\ 4\,H_2O$	$5.0 \cdot 10^{-3}$
$CoCl_2\ 6\,H_2O$	$1.0 \cdot 10^{-3}$
Thiamine	$0.1 \cdot 10^{-3}$

Carbon and nitrogen sources

the highly crystalline cellulose powder and the amorphous Walseth cellulose indicates, however, that high crystallinity of the substrate has a strong negative influence on the protein content of the mycelium. The low protein content of mycelium grown with mechanical waste fibers as a carbon source is certainly due to the presence of lignin, which considerably increases the complexity of the substrate.

When different celluloses are used as substrates, the enzyme activity shows a pattern which is the inverse of the protein concentration in the mycelium. Glucose and cellobiose do not induce cellulase production, but the activity increases from Walseth cellulose to the two types of cotton and is highest when cellulose powder is used as a carbon source. The low protein content of the mycelium must be a result of the fact that degradation of complex carbon sources requires a greater amount of enzymes. It seems obvious that the production of extracellular enzymes increases at the expense of the protein content of the mycelium. We have calculated that the extracellular protein is about 30% of the total synthesized protein. Of the extracellular protein, between 25 and 55% has been shown under different conditions to be endo- and exo-1,4-β-glucanases. Other enzymes necessary for the degradation of cellulose and hemicellulose certainly account for most of the remainder.

Most of our recent work has been concentrated on the conversion of waste fibers from a sulfite mill to protein. This carbon source gives 25–30% protein in the mycelium when it is grown batchwise. We are now using a 14-liter New Brunswick fermentor to determine parameters for a future scale-up. With this equipment we can control the agitation speed which influences the shear rate and the concentration of dissolved oxygen, which is continuously monitored and indicates the growth activity.

The oxygen consumption is periodically measured by turning off the inflow of air and noting the rate of decrease in oxygen concentration. The pH value is automatically controlled with addition of sulfuric acid and sometimes sodium hydroxide. Samples are taken out periodically and filtered to determine the dry weight of the mycelium or mycelium and cellulose. After drying at 80°C for 16 hr the filter cake is weighed, and the nitrogen content is determined by the Kjel-
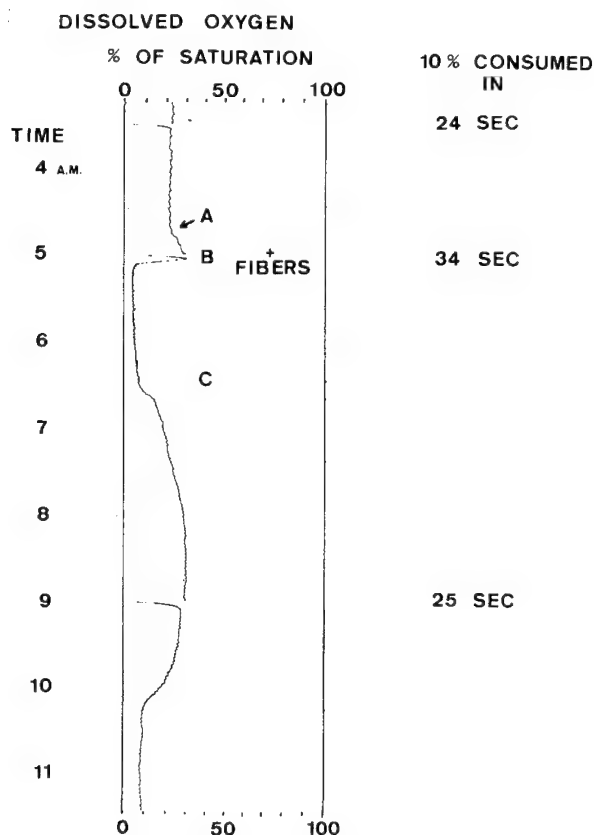
FIG. 2. Concentration of dissolved oxygen immediately before and after the first fiber addition, beginning at 20% oxygen saturation and at a consumption of 10% oxygen in 24 sec. At point A, low glucose concentration causes a decrease in oxygen consumption and an increase in the concentration of oxygen. At point B, fiber suspension replaces 2.5 liters of the growth medium; this causes a drastic increase in viscosity of the medium, resulting in a very low concentration of dissolved oxygen. At point C (1.5 hr after addition), oxygen concentration increases since the fibers are attacked such that the viscosity of the medium falls.

dahl method. The protein value here is normally so-called crude protein, that is 6.25 × total nitrogen. The filtrate is analyzed for reducing sugar using the Somogyi-Nelson method and the total carbohydrate is determined by the orcinol method. The endo-1,4-β-glucanase activity of the filtrate is determined by the viscometric method [8,9].

The composition of the medium is given in Table III. In most of our fermentations we have also added some yeast extract. This seems to speed up the germination which is also more complete. The yeast extract obviously contains a germination factor, as it is not needed during a continuous fermentation.

In shake-flask experiments it is possible to inoculate a fiber suspension with spores from agar plates, but if the same procedure is used in the fermentor very little growth is obtained. Our explanation is that a certain amount of mycelium is necessary to produce enough cellulases for hydrolysis of the insoluble polymers. In the fermentor, where all parameters are optimal, all spores germinate in 5–7 hr. The fungus initially uses easily degradable parts of the fibers. When this sub-

strate has been consumed, the fungus has to produce enough cellulases to liberate glucose from the more complex residue. Since the small cell mass cannot give high enough cellulase production, most of the formerly fast-growing mycelium begins to autolyze. To overcome these problems the cultivation is started on glucose, and the fibers are added when almost no glucose is left.

A rather long induction period might be expected before cellulases are produced when the substrate is changed from glucose to cellulose. This is, however, not the case as can be seen in Figure 2, which shows the concentration of dissolved oxygen immediately before and after the first fiber addition. The figure starts at 20% oxygen saturation and at a consumption of 10% oxygen in 24 sec. At point A, however, the glucose concentration is so low that the oxygen consumption begins to fall and the concentration of oxygen increases. At point B the consumption is 10% in 34 sec. Here 2.5 liters of the total 9.5 liters growth medium are replaced by fiber suspension. This causes a drastic increase of the viscosity of the medium, resulting in a very low concentration of dissolved oxygen. At point C, 1.5 hr after the addition, the oxygen concentration increases, since the fibers are attacked to such a degree that the viscosity of the medium falls again. This means that already after 1.5 hr enough cellulases are produced to give a measurable degradation of the fibers.

Under our fermentor conditions the fungus grows in pellet form. At a peripheral speed of about 2–2.5 m/sec of the turbine impeller, the diameter of the pellets is, however, only 0.2–0.4 mm. This is an advantage, since it lowers the viscosity of the broth and thus facilitates the aeration. The pellets are not big enough to give anaerobic zones in the center, and they are still easy to remove by filtration.

The fiber suspension contains 2–3% dry matter which makes is very difficult to pump in small volumes. This has so far prevented us from making the cultivation continuous. The technique now used is to take out about one-fourth of the medium and then add the corresponding amount of fiber suspension. By changing the intervals the resident time in this semicontinuous cultivation can be altered. In addition to the usual drawbacks with the discontinuous process, such as a lower productivity and changing growth conditions, a rather high viscosity is obtained after each addition with poor mixing and aeration as results. We are now developing a system with automatic addition four times an hour.

At a fungus concentration of 7–10 g/l. the production is about 350 mg mycelium/l./hr from chemical waste fibers at 39°C and pH 4.5. The protein production is about 95 mg protein/l./hr and simultaneously 640 mg of fibers are converted. These are average values, but the figures vary a great deal, probably due to the discontinuous character of the process which sometimes gives sporulation and other problems which influence the growth negatively. Even if the conversion is rapid, considering the complex substrate, it is not yet fast enough for an industrial process to be economical considering the protein prices today. A rough calculation points to a production cost of $400 per ton product with 25–30% protein in a 10,000 ton/yr plant. In this calculation the fiber cost is considered to be zero. In some cases the waste fibers have a negative value. The effluent from the cultivation has a concentration of reducing sugar of about 30 mg/l., and contains some excess phosphate and nitrogen. The effluent flow is about 45 m³ per ton of fibers converted.

To increase the yield of protein even with complex carbon sources we have tried to develop a symbiotic process involving the rot fungus *Sporotrichum pulveru-*

lentum and the common fodder yeast *Candida utilis*.   The results so far available demonstrate that such a process is possible.   No antagonism between the fungus and the yeast has been observed.   The yeast has been grown on substrates prepared from water and used fungus medium, respectively.   The culture solution from the fungus had only been sterile-filtered.   All compounds produced by the fungus were thus still present in the solution.   No difference in growth rate could be determined.   A corresponding experiment, where the fungus was grown in a medium where yeast had previously been grown, demonstrated that the yeast produced no compounds with a negative influence on the growth of the fungus.   On the contrary, the growth rate was enhanced, as the fungus spores germinated faster in the culture solution from the yeast.

Since both the fungus and the yeast grow excellently at pH 4.0–4.5 and temperatures around 35°C, it seems possible to develop a symbiotic process using the two organisms in combination.   The aim of such a process is that glucose freed by the fungus be primarily assimilated by the yeast.   This creates some problems which have to be solved.   In the first place, it is important to find conditions where the fungus grows slowly but still forms large amounts of cellulases.   At the same time, the yeast should grow rapidly, thereby increasing the protein content in the final cell-mass product.   The selection of strains must also be optimized.   It is not certain that a yeast is the best organism for the high protein component.   A mycelial fungus, such as *Paecilomyces varioti* might be better, since it would still give a filterable product.   Only under optimum conditions will the symbiotic process be economically feasible and advantageous compared with growth of the fungus alone.   The question is whether such conditions will be found for growth on solid, relatively difficultly degradable substrates, such as waste fibers.   The chances are probably greater when it comes to water-soluble oligomeric materials, such as occur in certain types of waste liquors.   In this case, still another technique can be utilized, namely, the technique of immobilized enzymes.   Further experiments have to be carried out concerning both the symbiotic process and the use of such enzymes.

REFERENCES

[1] K.-E. Eriksson and B. Pettersson, *Eur. J. Biochem., 51*, 193 (1975).
[2] K.-E. Eriksson and B. Pettersson, *Eur. J. Biochem., 51*, 213 (1975).
[3] K.-E. Eriksson, B. Pettersson, and U. Westermark, *FEBS Letters, 49*, 282 (1974).
[4] U. Westermark and K.-E. Eriksson, *Acta Chem. Scand., B28*, 204 (1974).
[5] U. Westermark and K.-E. Eriksson, *Acta Chem. Scand., B28*, 209 (1974).
[6] U. Westermark and K.-E. Eriksson, *Acta Chem. Scand., B29*, 419 (1975).
[7] K.-E. Eriksson and K. Larsson, *Biotechnol. Bioeng., 17* (3), 327 (1975).
[8] K. E. Almin and K.-E. Eriksson, *Biochim. Biophys. Acta, 139*, 238 (1967).
[9] K. E. Almin and K.-E. Eriksson, *Biochim. Biophys. Acta, 139*, 248 (1967).

PRODUCTION OF SUGARS FROM WASTE CELLULOSE BY ENZYMATIC HYDROLYSIS. I. PRIMARY EVALUATION OF SUBSTRATES

ROBERT K. ANDREN, MARY H. MANDELS, and
JOHN E. MEDEIROS

*U.S. Army Natick Development Center,
Natick, Massachusetts 01760*

SYNOPSIS

The problems of utilizing cellulose as a raw material for the production of chemicals are greatly simplified if it is first converted to glucose. This can be accomplished by either acid or enzymatic hydrolysis. At the Natick Laboratories we are developing a process for saccharifying waste cellulose with enzymes derived from the fungus Trichoderma viride. Waste cellulose is ball-milled and mixed at 10–30% concentration with the enzyme broth from a culture of the fungus grown on cellulose. The batch reactions are carried out at 50°C and a pH of 4.8. A 50% conversion of such materials as waste paper, cellulosic material from municipal trash, or high cellulose industrial and agricultural residues can be achieved in 6–24 hr yielding syrups of 5–15% concentrations. This paper reports on the availability and susceptibility of more than thirty representative cellulosic wastes. Each waste was tested with two enzyme preparations as received and after ball-milling in small batch reactors. Samples were removed and analyzed periodically over a 48-hr hydrolysis period. Composition of the sugar syrups was determined using high-performance liquid chromatography. The principal sugars found were glucose, cellobiose, and xylose. Most materials required ball-milling for satisfactory conversion. However, several samples including glassine, tissue mill, and Kraft Fiber paper-mill wastes, and hydropulped government documents, were readily saccharified as received. More extensive batch studies on these substrates were carried out, and their use in the fermentation media for enzyme production was investigated. Uses of the sugar syrups produced are also discussed.

INTRODUCTION

As earth's most abundant renewable organic chemical, the importance of cellulose as a potential source of fuel, food, and chemicals is becoming increasingly recognized. Tremendous quantities of waste cellulosic materials are available which can be broadly categorized as municipal wastes, industrial wastes (paper-mill effluents, sawdust, and sludges) and agricultural wastes (grasses, straws, bagasses, hulls, stalks, pomaces, etc.). While most such materials are currently burned, buried, or otherwise discarded, proper treatments could change them from liabilities into assets.

The possibilities of producing chemicals from cellulose, such as methanol by pyrolysis or methane gas by the action of anaerobic microorganisms, are well known. A process for direct conversion of cellulose in alkali-treated bagasse to single-cell protein using a cellulolytic bacterium has received considerable study including pilot-plant operations [1]. However, the utility of cellulose is greatly increased if it is first hydrolyzed to glucose and other sugars. These sugars can then be used as microbial substrates to produce a variety of fermentation chemicals (alcohols, solvents etc.) or single-cell protein, or they can serve as the base for the manufacture of organic chemicals.

It is possible to saccharify cellulose using either acid or enzymatic hydrolysis [2]. The enzymatic process offers the advantage of being carried out at moderate reaction conditions of pressure and temperature and is specific for cellulose, eliminating problems of producing unwanted by-products or reversion compounds. Recent developments have greatly improved the outlook for an enzymatic process using a mutant strain of the fungus *Trichoderma viride* [3]. To make the cellulosic substrates more susceptible to enzymatic attack, a variety of pretreatment processes have been studied [3]. Ball-milling, which increases the bulk density and surface area and most importantly reduces the crystallinity of the cellulose, has proven most effective in increasing reactivity. Saccharification of milled pure cellulose has been carried out successfully in a variety of reactor systems yielding 5–15% sugar syrups [4,5]. Batch studies using milled newspaper yielding 5–10% sugar solutions have also been reported [6]. However, the feasibility of this process must be proven by its application to a wide range of substrates.

This paper reports on the susceptibility to *Trichoderma* cellulase of 35 representative cellulosic wastes tested as received and after various milling treatments as small (5 g) samples. Composition of the syrups produced after 48-hr hydrolysis was analyzed by liquid chromatography. Two substrates, hydropulped government documents and a glassine paper waste, appeared particularly attractive because no milling pretreatment was required for good reactivity. These were tested further in 1-liter batch reactors with good results at several enzyme and substrate concentrations, and using three different hydrolysis temperatures. Our conclusions are that enzymatic hydrolysis of certain waste cellulosic materials is quite feasible. The sugar syrups, containing chiefly glucose, cellobiose, and xylose, will provide interesting new fermentation media or chemical feed stocks.

EXPERIMENTAL METHODS AND MATERIALS

Cellulosic Substrates Evaluated

1. A primary effluent sludge from a paper mill in northern Wisconsin produced at a rate of 10 tons/day. Estimated to be 80% cellulose. From Mr. John Cramsie, St. Regis Paper Co., New York, New York.

2. A glassine paper waste from Wisconsin coated with polyvinylidene produced in quantities of 10 tons/day. From Mr. Cramsie.

3. A glassine paper waste from Wisconsin coated with wax. Amounts up to 10 tons/day. From Mr. Cramsie.

4. A dried press cake produced by dewatering the residue (stillage) from distillation of fermented mash. Material has undergone screening, pressing, evapora-

tion and drying operations.   From Dr. H. A. Conner, National Distillers Products Co., Cincinnati, Ohio.

5. A mixture of wood and bark chips received from the Tennessee Valley Authority.

6. A waste straw from Oregon perennial rye grass used in grass-seed production.   From Mr. Raymond L. Weholt, Camran Corporation, Seattle, Washington.

7. A carbon paper waste from Frye Copysystems, Des Moines, Iowa.

8. A partially hydrolyzed cellulose produced from delinting cotton seed with mild sulfuric acid.   Somewhat depolymerized.   From Mr. Robert G. Wyeker, RAMCON, Memphis, Tennessee.

9. Newspaper which has passed through a hydropulper typical of those used in the food industry.   From Mr. Roger Williams, Hobart Manufacturing Co., Dedham, Massachusetts.

10. A sludge from the Coosa River Mill operation in Alabama; 65% passes through a 200 mesh screen.   From Mr. James Gresham, Kimerbly-Clark Corp., Neenah, Wisconsin.

11. Chemical pulp fines (short fibers) from Lakeville, Wisconsin tissue mill. Material originally at 2% solids is dewatered to 20% (76% cellulosic).   From Mr. Gresham.

12. An acid waste produced from treatment of cotton seeds with sulfuric acid to remove linters.   From Mr. Thomas Miles, Consulting Engineer, Beaverton, Oregon.

13. Oat Hulls which have been previously extracted with dilute acid to remove xylan.   From Dr. Peter Weinert, Hoffman-LaRoche Inc., Nutley, New Jersey.

14. A pulp generated by hydropulping classified documents at the Pentagon. Pure white pulp from DSA.   Approximately 20% dry solids.

15. Similar to above waste but contains manila materials imparting a yellowish coloration.   About 20% dry solids.

16. A paper-mill waste, 20% dry solids.   From Mr. Jerry Hagen, Cory Laboratories, Inc., Menominee, Michigan.

17. A paper-mill waste containing 12.6% dry solids.   From Mr. Hagen.

18. A dried corn fiber from a process stream at Staley's corn wet-milling plant. Normally contains 20–30% hemicellulose, 25–30% cellulose, 20% starch, 20% other.   From Mr. C. E. Ferguson, A. E. Staley Mfg. Co., Decatur, Illinois.

19. A waste cellulose and filler currently disposed of by land fill methods.   It contains an average of 90% cellulose.   From Mr. Ronald Benson, Nicolet Paper Company, DePere, Wisconsin.

20. Bleached kraft fibers used in the paper making process.   From Mr. Benson.

21. A bleached sulfite pulp used in making paper.   From Mr. Benson.

22. A sample of rye grass straw containing 46% cellulose, 16% lignins, and 25% pentosans.   From Mr. Miles.

23. A dried material (pomace) composed of grape skins, pulps, and seeds. From Mr. Bruce Wallin, Welch Food Inc., Westfield, New York.

24. Similar to #23 but containing no seeds.   From Mr. Wallin.

25. Material consisted of spent wood and bark chips.   From Mr. George Davis, Hercules Inc., Wilmington, Delaware.

26. A sample of the organic fraction of a municipal solids waste prepared by the ADL process.   From Mr. Thomas Lamb, Arthur D. Little Inc., Cambridge, Massachusetts.

27. A waste from *Alnus rubra*. Millions of tons of this material are produced annually. From Mr. James Kelso, International Wood Products Co., Los Angeles, California.

28. A pomace from grapes used in wine making. From Mr. Paul Kenney, Calona Wines Ltd., Kelowna, British Columbia, Canada.

29. A grape pomace from the Napa Valley Winery. Thousands of tons are produced annually. From Brother Alvan Maluvius, Mont LaSalle Wineyards, Napa, California.

30. A coarse wheat straw. From Mr. Floyd Horn, ARS, Fort Reno Livestock Research Station, El Reno, Oklahoma.

31. Common Sudan grass hay, a coarse straw from Mr. Horn.

32. A wheat straw which has been chopped through a Wiley Mill with a 1-mm screen. From Mr. Horn.

33. Bermuda grass #23, having passed through the Wiley Mill with a 1-mm screen. From Mr. Horn.

34. Summer morpa weeping lovegrass, having passed through a Wiley Mill with a 1-mm screen. From Mr. Horn.

35. Bermberg rayon fibers from a Cuprammonium treatment process. From Dr. Hillel Levinson, U.S. Army Natick Development Center, Natick, Massachusetts.

Production and Analysis of Enzyme

Methods used in these experiments have been described previously in detail [3]. The cellulase enzyme was produced by growing *Trichoderma viride* QM 9123 or QM 9414 in small laboratory fermentors on pure cellulose pulp (SW40) or on milled newspaper (NEP40). Culture broth was used directly for enzyme with pH adjustment to 4.8 using 0.05M citrate buffer and dilution or concentration (Amicon PM 30 Ultrafiltration membrane) to give the desired activity in the reactor. Cellulase activity was measured by incubating 0.5 ml of enzyme with 1.0 ml of buffer, and 50 mg of Whatman No. 1 filter paper for 1 hr at 50°C. The reducing sugar produced was measured as glucose by a DNS procedure. Enzyme units are expressed as micromoles of glucose produced/min in the above assay based on an enzyme dilution to give 2.0 mg of glucose. Protein was measured by the Lowry procedure after precipitation with 5% trichloracetic acid.

Substrate Evaluation

Substrate evaluations were carried out with 5 g (dry weight) of substrate plus 95 ml of enzyme solution in shake flasks and incubated at 50°C. Where sugar was present in the substrate a blank was run without enzyme, and appropriate corrections were made. The reducing sugar was measured by a DNS procedure on aliquots of the suspension as hydrolysis proceeded. Saccharification of this 5% slurry equals glucose mg/ml × 1.8 [3].

All results are expressed relative to Sweco ball-milled newspaper run under identical conditions. Substrates were run as received and after drying at 80°C if wet. If upon drying the sample was of a substantial particle size it was passed

through the 0.25- and 0.20-inch screens in the U6 Fitzpatrick hammer mill. Part of the 0.25 fraction was also ball-milled (porcelian lab mill) and tested.

One-Liter Batch Saccharification

One-liter batch saccharifications were carried out at a pH of 4.8 in a 2-liter jar stirred at 200 RPM and immersed in a water bath for temperature control [6]. The bulk density of the substrates used did not permit evaluation of concentrations greater than 7.5% solids in the reactor. Reaction conditions for these runs are summarized in Tables II and III.

Composition of Syrups

Composition of the sugars produced was determined using high-performance liquid chromatography [7,8]. Components were separated on a 30-cm-by-4-mm OD MicroBondapak Carbohydrate column (Waters Associates), and the sugars were detected by a Waters Model R401 Differential Refractometer. The carrier solvent, 75% Acetonitrile and 25% Water, was pumped at approximately 4 ml/min with a Waters Model 6000 Solvent Delivery System. A DuPont 834 Automatic Sampling and Injection System allowed for analysis of 96 consecutive samples with the system unattended. Excellent separation and resolution of peaks were attained and the time between injections reduced to approximately 8 min.

RESULTS

Substrate Evaluations

Results of the substrate evaluations are shown in Table I. The samples are presented in order of decreasing reactivity and have somewhat arbitrarily been divided into four groups based on their susceptibility to enzymatic saccharification, relative to ball-milled newspaper. While some overlapping might be noted, the general characterization of the materials in each group are:

Group	Relative Saccharification at 48 Hr
I. Excellent	>0.85 as received
II. Good	>1.0 when laboratory ball-milled
III. Fair	0.5–1.0 when laboratory ball-milled
IV. Poor	<0.5 when laboratory ball-milled

Also shown in Table I are the enzyme and soluble-protein concentrations in the reactor during hydrolysis and the DNS analysis of the 48-hr samples. Each sample was run in the "as received" (wet or dry) condition and after a variety of milling treatments. In general, substrates which were produced or received wet, lost considerable reactivity when dried. Upon drying there is an increase in the crystallinity of the cellulose. The quantity of cellulose and its degree of crystallinity in each substrate are the greatest factors in determining its susceptibility to enzymatic hydrolysis. While hammer-milling may indeed decrease the particle size

with a resulting increase in surface area, results show only marginal increases in reactivity over unmilled substrates (Table I). It is ball-milling which is energy intensive enough to reduce the crystallinity and allow water and enzyme to penetrate into the fibril substructure and hydrolyze the cellulose. Ball-milling makes the

TABLE I

Hydrolysis of Cellulosic Substrate by Cellulase Enzymes[a]

SUBSTRATE & PRETREATMENT	ENZYME ACTIVITY units/ml	SOLUBLE PROTEIN mg/ml	48 HR HYDROLYSIS SAMPLES SACCHARIFICATION (DNS METHOD)	TOTAL REDUCING SUGARS (DNS) mg/ml	SACCHARIFICATION RELATIVE TO SWECO NP 1 HR	4 HR	24 HR	48 HR	COMPOSITION OF SUGARS AT 48 HRS HYDROLYSIS mg/ml GLUCOSE	CELLOBIOSE	XYLOSE	TOTAL SUGARS
GROUP I												
Excellent												
NICOLET SULFITE PULP (22)												
Undried	1.3	1.6	103.1	57.6	.96	1.1	1.7	2.5	—	—	—	—
Jay Bee	1.3	1.6	65.9	36.6	.80	.71	1.2	1.6	25.9	7.1	1.5	34.5
Hammer - .25	1.3	1.6	25.5	41.9	.85	.83	1.3	1.6	27.0	6.7	.3	34.6
Ball Milled	1.3	1.6	94.9	—	1.4	2.0		2.3	—	—	—	—
BERYBERG RAYON FIBER (36)												
Undried	1.6	1.8	72.0	40.0	.68	1.15	1.75	1.81	23.2	12.0	.5	35.6
Ball Milled	1.6	1.8	40.0	22.0	.33	.46	.86	1.01	15.0	5.6	.2	20.9
HYDROPULPED GOVT. DOC-W (19)												
Undried	1.3	1.6	77.2	42.9	.92	.93	1.2	1.3	32.3	0.0	4.7	37.0
Dried	1.3	1.6	54.2	33.1	.86	.77	1.1	1.3	—	—	—	—
Ball Milled	1.3	1.6	68.9	38.3	1.4	1.5	1.5	1.6	30.5	1.5	4.7	36.7
TISSUE MILL WASTE (12)												
Undried	.84	1.4	52.0	28.9	1.3	.96	1.1	1.3	20.8	1.9	1.8	24.4
Dried	.84	1.4	54.9	30.5	.74	.70	1.1	1.4	20.5	2.5	3.5	26.5
Ball Milled	.84	1.4	51.7	28.7	.77	.75	—	1.3	19.5	5.8	3.5	28.6
CARBON PAPER WASTE (7)												
Jay Bee	.84	1.4	48.2	26.8	.70	.79	.81	1.2	18.2	1.2	2.0	21.5
Ball Milled	.84	1.4	43.7	24.3	.83	.80	.74	1.1	15.0	2.9	1.8	20.2
HYDROPULPED GOVT DOC-W/Y (16)												
Undried	1.3	1.6	55.3	30.7	.91	.84	1.2	1.3	22.8	1.5	3.3	27.6
Dried	1.3	1.6	55.6		.83	.74	1.1	1.3	—	—	—	—
Ball Milled	1.3	1.6	78.8	43.8	1.3	1.4	1.7	1.8	35.1	2.1	5.1	42.3
ST. REGIS PAPER SLUDGE(1)												
Undried	.84	1.4	64.8	36.0	.7	.9	1.08	.97	23.9	4.2	1.4	29.5
Dry	.84	1.4	52.6	29.2	.51	.72	.71	.79	18.0	1.7	.75	20.5
Ball Milled	.84	1.4	62.6	34.8	.87	.96	.90	.93	23.9	2.5	1.0	27.4

SUBSTRATE & PRETREATMENT	ENZYME ACTIVITY units/ml	SOLUBLE PROTEIN mg/ml	48 HR HYDROLYSIS SAMPLES SACCHARIFICATION (DNS METHOD)	TOTAL REDUCING SUGARS (DNS) mg/ml	SACCHARIFICATION RELATIVE TO SWECO NP 1 HR	4 HR	24 HR	48 HR	COMPOSITION OF SUGARS AT 48 HRS HYDROLYSIS mg/ml GLUCOSE	CELLOBIOSE	XYLOSE	TOTAL SUGARS
ST. REGIS PVO GLASSINE PAPER (2)												
Dry	.84	1.4	56.2	31.2	.92	.61	.74	.84	22.8	2.3	2.2	27.4
Ball Milled	.84	1.4	62.6	34.8	.76	.70	.80	.93	24.5	1.25	1.8	27.5
NICOLET WATE FILLER (20)												
Undried	1.3	1.6	39.2	19.0	1.1	1.1	.71	.95	10.0	6.3	1.5	17.8
Dried	1.3	1.6	27.7	15.4	.71	.61	.67		2.1	2.5	0.0	4.6
Ball Milled	1.3	1.6	54.9	30.5	1.1	1.3	1.1	1.3	15.7	9.0	1.0	25.7
NICOLET KRAFT PULP (21)												
Hammer - .25"	.84	1.4	45.9	25.3	.62	.68	.78	.94	14.6	1.7	1.8	19.1
Ball Milled	.84	1.4	76.5	42.5	1.08	1.26	1.43	1.57	25.7	1.1	2.9	29.7
GROUP II												
GOOD												
COTTON LINTERS MILES (13)												
Dry	.64	.75	8.5	4.7	.02	.09	.15	.23	2.6	.4	.8	3.7
Ball Milled	.64	.75	68.0	37.8	1.9	1.9	1.2	1.2	23.9	11.7	.5	36.1
EXTRACTED OAT HULLS (14)												
Dry	.84	1.4	7.9	4.4	.3	.2	.16	.20	—	—	—	—
Ball Milled	.84	1.4	59.9	33.3	1.25	1.06	1.25	1.50	21.7	2.5	3.0	33.3
COOSA PAPER WASTE (10)												
Undried	.84	1.4	27.9	15.5	.85	.73	.64	.72	10.5	0.0	.6	11.2
Dried	.84	1.4	20.0	11.1	.34	.46	.39	.51	7.7	0.0	.4	9.1
Ball Milled	.84	1.4	24.3	13.5	.85	.77	.56	.62	11.3	0.0	1.0	12.3
COBY PAPER MILL WASTE(18)												
Undried	1.3	1.6	24.0	13.3	.41	.48	.53	.53	8.0	2.1	1.3	11.3
Dried	1.3	1.6	23.3	13.0	.35	.30	.30	.56	9.1	.4	2.3	11.9
Ball Milled	1.3	1.6	53.0	29.4	.71	1.4	1.3	1.3	21.4	1.9	4.3	27.5
HERCULES WOOD CHIPS (26)												
Hammer - .25"	1.5	1.3	4.0	2.2	.16	.11	.10	.11	.8	.1	.2	1.1
Hammer - .02"	1.5	1.3	7.6	4.2	.32	.22	.19	.21	3.0	—	.9	3.9
Ball Milled	1.5	1.3	37.8	26.0	.98	.95	1.00	1.02	11.0	4.3	1.7	17.0

maximum amount of cellulose available for enzymatic attack and gives a good indication of the total amount of cellulose in the material.

The three primary sugars produced from most of the cellulosic substrates were glucose, cellobiose, and xylose. These account for more than 90% of the total.

TABLE I (*continued*)

SUBSTRATE & PRETREATMENT	ENZYME ACTIVITY units/ml	SOLUBLE PROTEIN mg/ml	48 HR HYDROLYSIS SAMPLES % SACCHARIFICATION	TOTAL REDUCING SUGARS (DNS) mg/ml	SACCHARIFICATION RELATIVE TO SWECO NP 1 HR	4 HR	24 HR	48 HR	COMPOSITION OF SUGARS AT 48 HRS HYDROLYSIS mg/ml GLUCOSE	CELLOBIOSE	XYLOSE	TOTAL SUGARS
UNPROCESSED WHEAT STRAW (31)												
Dry	1.1	1.6	12.6		.26	.23	.29	.25	4.2	0.0	.9	5.1
Ball Milled	1.1	1.6	45.0	25.0	1.48	1.36	.97	.92	13.1	1.5	6.4	21.0
OREGON RYE STRAW (23)												
Hammer - .25"	1.3	1.6	18.5	10.3	.31	.28	.30	.43	5.4	0.0	.7	6.1
Hammer - .02"	1.3	1.6	17.6	9.8	.41	.33	.37	.41	—	0.0	—	—
Ball Milled	1.3	1.6	46.8	26.0	1.4	.93	.93	1.1	25.6		.7	26.3
COTTON SEED LINTERS (8)												
Dry	.84	1.4	5.2	2.9	.09	.15	.09	.13	1.8	14.0	0.0	2.3
Ball Milled	.84	1.4	47.7	26.5	.86	1.0	.87	.22	22.8	1.0	0.0	23.8
CORY PAPER MILL WASTE (17)												
Undried	1.3	1.6	33.1	18.4	.74	.56	.63	.77	14.9	0.0	2.6	17.4
Dried	1.3	1.6	25.0	13.9	.62	.40	.50	.60	—	0.0	—	—
Ball Milled	1.3	1.6	44.3	24.6	1.1	.92	.91	1.0	20.5		4.2	24.7
SUDAN GRASS HAY (32)												
Dry	1.1	1.6	22.7	12.6	.65	.40	.52	.46	7.2	.3	.9	8.4
Ball Milled	1.1	1.6	40.0	22.0	1.81	1.23	1.00	.82	9.9	.6	3.3	13.9
GROUP III **FAIR**												
ST. REGIS GLASSINE PAPERWAX (3)												
Dry	.64	.75	50.8	28.2	.50	.62	.84	.76	19.3	2.5	1.0	22.9
Ball Milled	.64	.75	58.3	32.4	.46	.66	.63	.87	18.4	2.7	1.1	22.2
WELCH'S SEEDLESS GRAPE POMACE (25)												
Hammer - .25"	.84	1.4	29.2	16.2	.52	.40	.46	.47	10.0	.1	.4	10.5
Hammer - .02"	.84	1.4	16.8	16.8	.72	.98	.99	.99	11.0	0.0	0.0	11.0
Ball Milled	.84	1.4	27.0	27.0	.97	.80	.77	.87	15.4	1.0	1.9	18.3

SUBSTRATE & PRETREATMENT	ENZYME ACTIVITY units/ml	SOLUBLE PROTEIN mg/ml	48 HR HYDROLYSIS SAMPLES % SACCHARIFICATION (DNS METHOD)	TOTAL REDUCING SUGARS (DNS) mg/ml	SACCHARIFICATION RELATIVE TO SWECO NP 1 HR	4 HR	24 HR	48 HR	COMPOSITION OF SUGARS AT 48 HRS HYDROLYSIS mg/ml GLUCOSE	CELLOBIOSE	XYLOSE	TOTAL SUGARS
STALEY CORN FIBER (19)												
Hammer - .25"	.84	1.4	18.4	10.2	.27	.40	.31	.40	—	—	—	—
Hammer - .02"	.84	1.4	19.3	10.7	.41	.38	.33	.42	—	—	—	—
Ball Milled	.84	1.4	35.1	19.5	1.1	.68	.40	.76	—	—	—	—
ALDER WOOD WASTE (28)												
Dry	.84	1.4	3.8	2.1	.14	.08	.08	.07	2.1	2.1	.1	2.2
Ball Milled	.84	1.4	30.2	16.8	.83	.52	.58	.62	11.7	11.7	0.0	14.6
WELCH'S GRAPE POMACE (24)												
Hammer - .25"	.84	1.4	23.8	13.2	.25	.32	.34	.35	6.9	0.0	.54	7.5
Ball Milled	.84	1.4	35.6	19.8	.76	.55	.56	.59	12.2	0.0	0.0	12.2
ADL SOLID WASTE (27)												
Dry	.84	1.4	11.5	6.4	.20	.19	.22	.24	1.4	4.9	.7	7.0
Ball Milled	.84	1.4	27.0	15.0	.42	.37	.46	.55	2.3	9.8	1.8	13.9
RYE GRASS STRAW (6)												
Hammer - .25"	.84	1.4	18.7	10.4	.29	.29	.28	.28	6.0	.8	.2	7.1
Hammer - .02"	.84	1.4	19.4	10.8	.41	.32	.27	.29	5.4	0.0	.4	5.8
Ball Milled	.84	1.4	31.7	17.6	.72	.53	.45	.47	10.3	1.7	1.6	13.6
BERMUDA GRASS (34)												
Dry	1.1	1.6	27.5	15.3	.83	.65	.60	.56	5.7	1.1	1.1	7.8
BOAT STAGE WHEAT (33)												
Dry	1.1	1.6	22.0	12.0	.49	.51	.48	.45	.7	5.0	.8	6.5
GROUP IV **POOR**												
DISTILLER'S GRAIN (4)												
Dry	.84	1.4	20.9	11.6	.33	.77	.23	.24	6.4	0.0	4.0	10.4
Ball Milled	.84	1.4	24.1	13.4	.42	.39	.25	.29	7.1	0.0	0.0	7.1
SUMMER MORPA LOVEGRASS (35)												
Dry	1.1	1.6	14.6	8.1	.34	.33	.33	.36	4.7	0.0	.5	5.2

TABLE I (*continued*)

SUBSTRATE & PRETREATMENT	ENZYME		48 HR HYDROLYSIS SAMPLES		SACCHARIFICATION RELATIVE TO SWECO N				COMPOSITION OF SUGARS AT 48 HRS HYDROLYSIS mg/ml			
	ACTIVITY units/ml	SOLUBLE PROTEIN mg/ml	SACCHARIFICATION (DNS METHOD)	TOTAL REDUCING SUGARS (DNS) mg/ml	1 HR	4 HR	24 HR	48 HR	GLUCOSE	CELLOBIOSE	XYLOSE	TOTAL SUGARS
CHRISTIAN BROTHERS POMACE (30)												
Hammer - .25"	1.1	1.6	11.2	6.2	.09	.17	.19	.16	2.6	0.0	0.0	2.6
Hammer - .02"	1.1	1.6	13.3	7.4	.20	.24	.28	.20	2.5	0.0	0.0	2.5
Ball Milled	1.1	1.6	16.2	9.0	.13	.33	.27	.26	2.8	.3	.2	3.4
GALLO WINES GRAPE POMACE (29)												
Hammer - .25"	1.6	1.8	11.5	6.4	.13	.18	.21	.21	3.8	.2	.1	4.1
Hammer - .02"	1.6	1.8	11.5	6.4	.37	.33	.24	.21	3.4	0.0	0.0	3.4
Ball Milled	1.6	1.8	12.2	6.8	.66	.50	.33	.22	3.2	.2	.2	3.6
HOBART MILLED NEWSPAPER (9)												
Undried	.84	1.4	3.8	2.1	.66	.44	.36	.10	0.0	0.0	0.0	0.0
Dried	.84	1.4	—	.8	.33	.30	.25	—	0.0	0.0	.38	.4
Ball Milled	.84	1.4	9.5	5.3	.56	.46	.30	.24	1.0	0.1	.25	2.7
TVS WOOD WASTE (5)												
Hammer - .25"	.84	1.4	2.5	1.4	.03	.03	.04	.04	1.1	0.0	.5	1.6
Ball Milled	.84	1.4	11.2	6.2	.23	.19	.17	.16	3.8	0.0	.5	4.3

[a] Samples were, evaluated at 5% dry wt in 6 tests. Enzyme activities and protein concentrations in the reactor are indicated % saccharification equals reducing sugars (mg/ml) × 1.8. All saccharification values are expressed relative to ball milled newspaper (1.0) run in the same test with the same enzyme preparation. Glucose, cellobiose, and xylose values by liquid chromatography. Total reducing sugar by DNS as glucose. All % saccharification are based on the total weight of substrate including noncellulosic impurities.

TABLE II
Summary Table for 1 1. Batch Hydrolysis of Hydropulped Government Documents

EXPERIMENT NUMBER	SUBSTRATE SAMPLE #	SUBSTRATE CONCENTRATION WEIGHT	ENZYME SOLUBLE PROTEIN [a] mg/ml	ENZYME CONCENTRATION UNITS/ml	TEMP. °C	SUGAR CONCENTRATION AFTER 24 HOURS (DNS) mg/ml	SACCHARIFICATION AFTER 24 HOURS [b]
1	15	2.5	0.8	0.5	50	16.2	64
2	16	5.0	0.8	0.5	50	23.1	43
3	16	7.5	0.8	0.5	50	25.5	33
4	16	2.5	1.6	1.0	50	19.9	77
5	16	5.0	1.6	1.0	50	33.0	60
6	16	7.5	1.6	1.0	50	38.5	47
7	16	2.5	2.4	1.5	50	21.2	79
8	16	5.0	2.4	1.5	50	38.5	67
9	16	7.5	2.4	1.5	50	46.0	53
10	15	5.0	1.6	1.0	45	28.1	54
11	15	5.0	2.4	1.5	45	32.7	59
12	15	5.0	1.6	1.0	55	29.6	54
13	15	5.0	2.4	1.5	55	33.0	61

[a] All enzyme from T.V. grown on pure cellulose.

[b] % saccharification $= \dfrac{\text{Glucose (mg/ml)} \times .9}{\text{Substrate (mg/ml)}} \times 100$

TABLE III
Summary Table for 1 1. Batch Hydrolysis of Glassine PVD Waste

EXPERIMENT NUMBER	SUBSTRATE SAMPLE #	SUBSTRATE CONCENTRATION WEIGHT %	ENZYME SOLUBLE PROTEIN mg/ml	ENZYME CONCENTRATION UNITS/ml	TEMP. °C	SUGAR CONCENTRATION AFTER 24 HOURS (DNS) mg/ml	SACCHARIFICATION AFTER 24 HOURS[b] %
1	2	5.0	0.7	0.5	50	17.7	32
2	2	5.0	1.5	1.0	50	24.1	43
3	2	5.0	2.2	1.5	50	24.3	44
4	2	7.5	0.7	0.5	50	18.8	23
5	2	7.5	1.5	1.0	50	29.6	36
6	2	7.5	2.2	1.5	50	33.4	40
7	2	7.5	1.5	1.0	55	31.8	38
8	2	7.5	2.2	1.5	55	40.0	48
9	2	7.5	1.5	1.0	45	36.0	43
10	2	7.5	2.2	1.5	45	44.5	53

[a] All enzyme from T.V. grown on pure cellulose.

[b] % saccharification $= \dfrac{\text{Glucose (mg/ml)} \times .9}{\text{Substrate (mg/ml)}} \times 100$

The chromatograms do indicate the presence of small quantities of several other sugars depending on the substrate used. While they have not all as yet been identified, work is proceeding in this area. The quantities of the three main sugars and their totals are shown in Table I. In most cases the DNS total was higher. Reasons for this include the presence of the unidentified sugars and the fact that glucose served as the single standard for the DNS method [8].

Group I

The substrates in this group were extremely reactive without additional pretreatments. They consisted mainly of paper-mill wastes or pulps and wastes produced by hydropulping such as classified government documents from the Pentagon. The paper-mill wastes have already undergone a variety of physical (beating, grinding) and chemical (sulfite pulping) processes, resulting in their high susceptibility to enzymatic attack. Their cellulose content is also greater than many of the other municipal and agricultural wastes. Most of these materials are produced wet and upon drying lose much of their reactivity. This could be restored by ball-milling. The primary sugar produced was glucose with the St. Regis and Nicolet wastes yielding some quantities of cellobiose. Since milling is currently a major process cost and large quantities of these waste products are available, this group certainly presents favorable economics with regard to eventual scale-up possibilities.

Group II

This group of substrates can roughly be compared to newspaper in reactivity. Ball-milling or other pretreatment is necessary to make the cellulose available for

enzymatic hydrolysis. This has a major impact on the process economics. The more susceptible materials in this group were again paper-mill wastes. Ball-milling of these produces only about a 20–30% increase in reactivity. Cotton linters being almost pure crystalline cellulose are very unreactive as received. Ball-milling produced a 10-fold increase in saccharification. The oat hulls responded in a similar manner. The straws and hay in this group contained about the same quantity of cellulose as newspaper and required ball-milling. Somewhat offsetting its relatively high cost, ball-milling increases the bulk density and allows the use of fairly high solids concentrations (15–20%) in the hydrolysis reaction.

Group III

Group III is composed almost entirely of agricultural materials, which easily represents the largest class of available cellulosic wastes. Their lesser susceptibility is due both to crystallinity and to the considerable content of noncellulosics. Significant increases in saccharification are realized by ball-milling which would be necessary in any large-scale utilization of these substrates.

Group IV

The materials in this group had very low susceptibility to enzymatic hydrolysis even after ball-milling. One major reason is their low cellulosic content. It is unlikely that saccharification of these substrates would be economically feasible.

RESULTS OF ONE-LITER BATCH SACCHARIFICATION

Hydropulped Government Documents

This is an excellent substrate, being very reactive as received. It is doubtful that economics would justify any additional pretreatment. Saccharification of 2.5–7.5% slurries with 0.5–1.5 units/ml of cellulase at 50°C yielded 1.6–4.6% sugar solutions at 24 hr representing 33–77% saccharification (Table II). As substrate concentration increased the amount of glucose increased, and percent saccharification decreased. As enzyme concentration increased both glucose level and percent saccharification increased. (Fig. 1). Saccharification was optimum at 50°C. At 45 or 55°C saccharification was reduced (Fig. 2). As expected (Fig. 3), glucose was the primary sugar with low levels of xylose and cellobiose produced.

Glassine Waste, Polyvinylidine Coated

This is another excellent substrate that does not require pretreatment. Saccharification of 5 and 7.5% slurries with 0.5–1.5 units/ml of cellulase at 50°C yielded 1.8–4.5% sugar at 24 hr, representing 32–44% hydrolysis (Table III). As with the hydropulped documents, glucose concentration increased with increasing
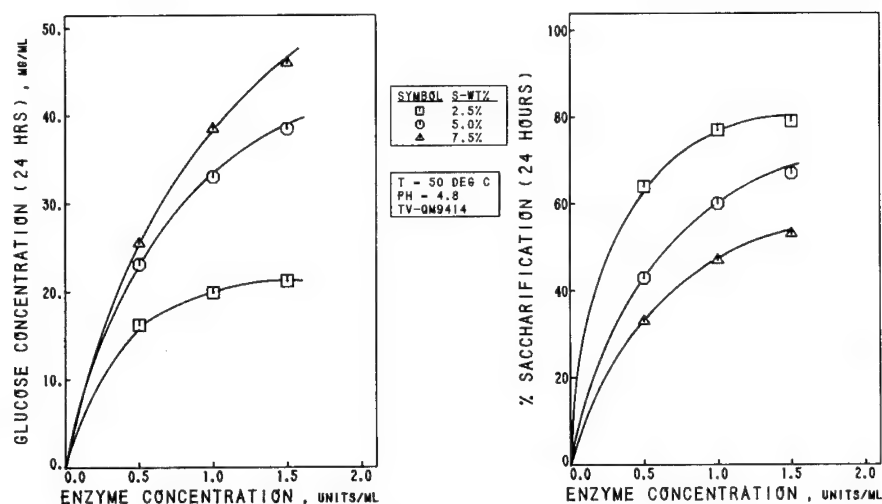
FIG. 1. One-liter batch hydrolysis: hydropulped grovernment documents (sample numbers 15 and 16). Plots of enzyme concentration vs. glucose concentration after 24 hr (left) and enzyme concentration vs. percent saccharification after 24 hr (right). As enzyme concentration increased, so did glucose level and percent saccharification. □ 2.5 wt-%; ⊙ 5.0 wt-%; ▲ 7.5 wt-%; temperature, 50°C; pH, 4.8; *Trichoderma viride* strain, QM9414.
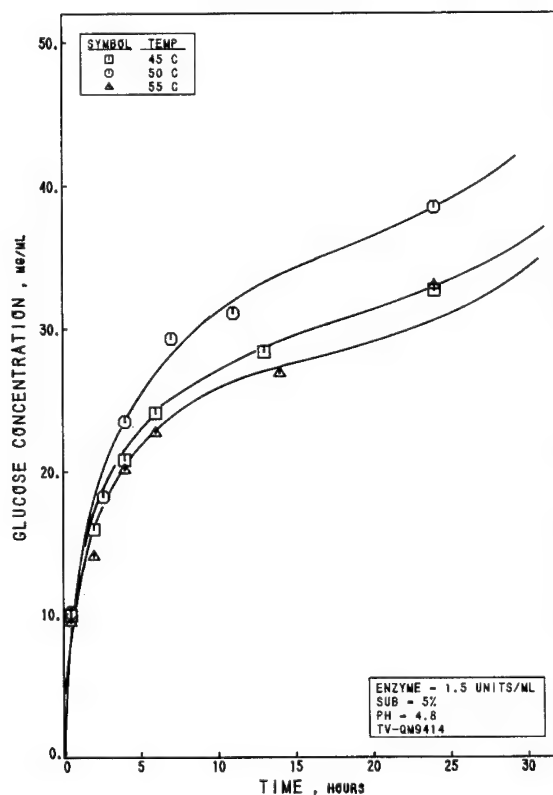
FIG. 2. One-liter batch hydrolysis: hydropulped government documents (sample numbers 15 and 16). Plots of time vs. glucose concentration (maximum saccharification at 50°C): □ 45°C; ⊙ 50°C; Δ 55°C; enzyme, 1.5 unit/ml; substrate concentration, 5%; pH, 4.8; *Trichoderma viride* strain, QM9414.
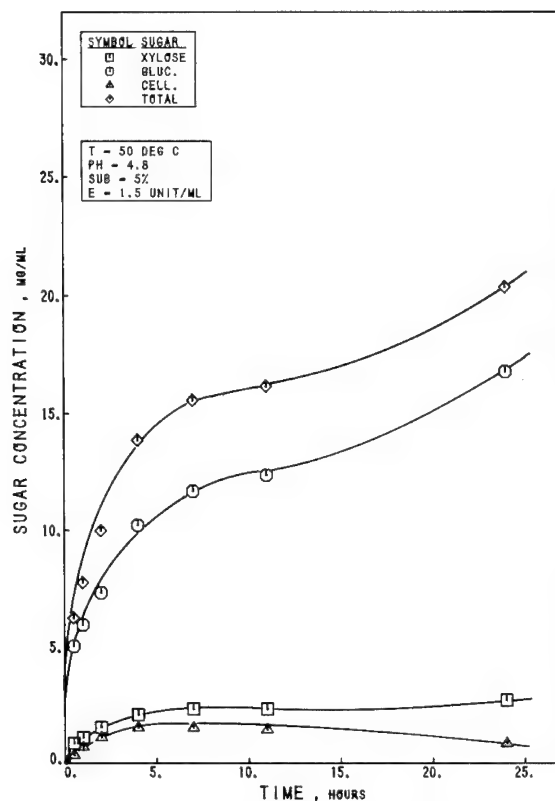
FIG. 3. Composition of sugars produced during hydrolysis of hydropulped government documents. Plot of time vs. sugar concentration showing glucose to be the primary sugar: ▢ xylose, ⊙ glucose; △ cellulose; ◇ total; temperature, 50°C; pH, 4.8; substrate concentration, 5%; enzyme, 1.5 unit/ml.
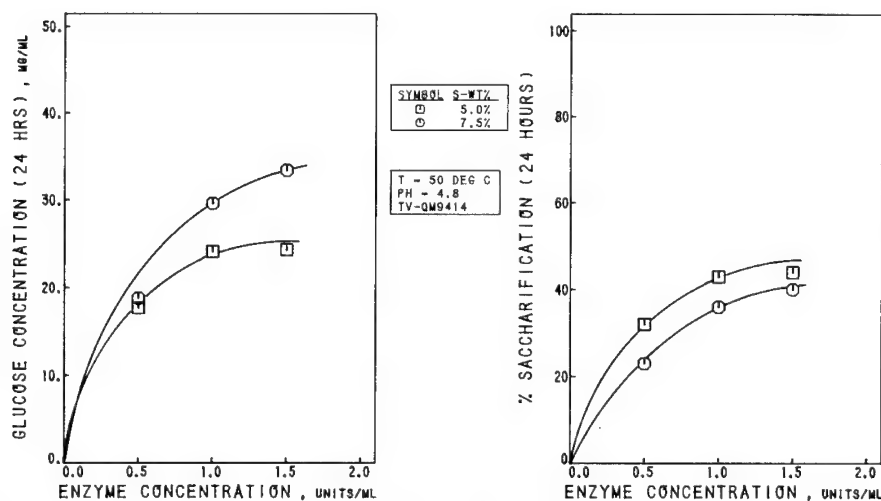
FIG. 4. One-liter batch hydrolysis: glassine-polyvinylidine paper waste (sample number 2). Plots of enzyme concentration vs. glucose concentration after 24 hr (left) and enzyme concentration vs. percent saccharification after 24 hr (right). Both glucose concentration and percent saccharification increased with increasing enzyme concentration: ▢ 5.0%; ⊙ 7.5%; temperature, 50°C; pH, 4.8; *Trichoderma viride* strain, QM9414.
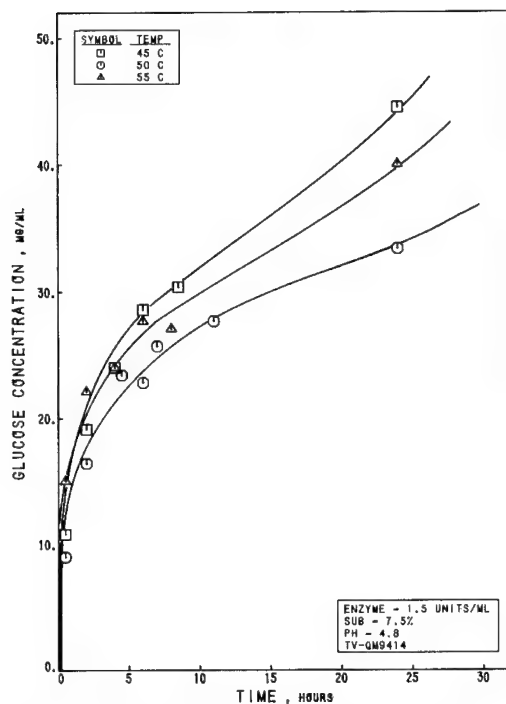
FIG. 5 Hydrolysis of glassine-polyvinylidine paper waste (sample number 2). Plot of time vs. glucose concentration. Less glucose was produced at 50°C than at other temperatures. ⊡ 45°C; ⊙ 50°C; ⊿ 55°C; enzyme, 1.5 unit/ml; substrate concentration, 7.5%; pH, 4.8; *Trichoderma viride* strain, QM9414.

substrate concentration and percent saccharification declined, but both glucose concentration and percent saccharification increased with increasing enzyme concentration (Fig. 4). A peculiar temperature effect was noted with more sugar produced at 45 or 55°C than at 50°C (Fig. 5). This may be related to temperature effects on either the polyvinylidine which was used to coat the glassine paper or on the polyvinyl alcohol used as plasticizer. Supernatants taken at 45 or 55°C in this experiment became turbid after freezing, and the 50°C supernatants contained large blobs after freezing and thawing. It is of interest to note that the wax-coated glassine waste was less reactive after ball-milling than after only shredding. (Table I). We assume that this is due to wax being pounded into the cellulose during ball-milling. As with the hydropulped documents glucose was the primary product of saccharification (Fig. 6). The cellobiose level reached a point of maximum concentration (.7%) and then decreased as the rate of its decomposition exceeded the rate of formation. Xylose was a minor component that appeared early in the hydrolysis.

CONCLUSIONS

The enzymatic hydrolysis of cellulose to sugars is a feasible method for converting a renewable organic chemical resource to useful products. While some cellobiose and xylose are produced, the primary component of the syrups is glucose.
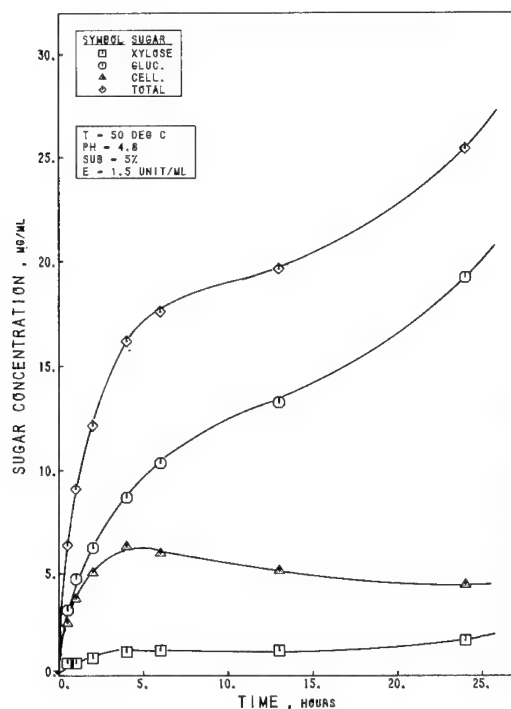
FIG. 6. Composition of sugars produced during hydrolysis of glassine-polyvinylidine waste. Plot of time vs. sugar concentration. Glucose is the primary product of saccharification. ▣ xylose; ⊙ glucose; △ cellulose; ◊ total; temperature, 50°C; pH, 4.8; substrate concentration, 5%; enzyme, 1.5 unit/ml.

It has been shown that a wide variety of cellulosic wastes can be enzymatically saccharified. While more than 50 substrates have been evaluated in this and previous studies, many more are available.

Paper-mill wastes are most susceptible to enzymatic degradation due to their high cellulose content and the chemical and physical treatments they undergo during the papermaking process. In general, agricultural materials require ball-milling to break down the crystalline cellulose and make it available for saccharification. This may not be necessary if the material is being treated for purposes other than saccharification (such as removing color from grape skin, evaluating forages or decreasing the energy required in pulping).

Considerable work remains to be done in the area of pretreatment. Ball-milling is both expensive and energy intensive. Other physical, chemical or combination treatments could improve the process economics greatly.

Cellulose tends to be adsorbed by both the cellulosic and noncellulosic fractions of the tested substrates. Investigations of methods of desorption and recovery of these enzymes to lower process costs are needed.

The sugars produced from waste cellulose will be valuable raw materials. Much of our attention has focused on glucose, the major product. This sugar is suitable for human or animal food. Glucose grown microorganisms such as yeast could be a valuable single-cell protein food for animals or even man. Glucose can be converted by microorganisms to citric acid, gluconic acid, ascorbic acid and many other microbial fermentation products. One of these is ethanol a valuable fuel or chemical raw material [9]. The utilization of cellobiose, xylose and other

sugars will pose research challenges and opportunities. Some organisms such as Candida yeasts can utilize these sugars as well as the glucose for production of SCP, ethanol, or other fermentation products. Interesting new fermentations based on these sugars can no doubt be developed. Cellobiose may find value in food applications such as slow release of sugar in the baking industry or capitalizing on its nonsweet, nonbrowning properties in food texturizing or low-moisture foods. Xylose is a raw material for furfural production and a substrate for glucose isomerase production.

The most pressing requirement for further development and practical application of enzymatic saccharification of cellulose is a thorough elucidation of the economics of the complete process. This is a major goal of the pilot studies now being carried out at the U.S. Army Natick Development Center.

REFERENCES

[1] V. P. Srinivasan and Y. W. Han, *Adv. Chem Ser., 95,* 447 (1969).

[2] E. T. Reese, M. Mandels, and A. Weiss, *Advan. Biochem. Eng., 2,* 181 (1972).

[3] M. Mandels, L. Hontz, and J. M. Nystrom, *Biotech. Bioeng., 16,* 1471 (1974).

[4] M. Mandels, J. Kostick, and R. Parizek, *J. Polym. Sci. C, 36,* 445 (1971).

[5] T. K. Ghose and J. Kostick, *Biotech. Bioeng., 12,* 921 (1970).

[6] D. Brandt, L. Hontz, and M. Mandels, *AIChE J. Symp. Ser., 69* (133), 127 (1973).

[7] J. K. Palmer, *Analytical Letters, 8,* 215 (1975).

[8] J. K. Palmer, this volume, p. 000.

[9] I. S. Goldstein, NSF-RANN Report, Dept. Wood & Paper Science. (1974).

[10] A. J. Stamm, *Proc. Amer. Phil. Soc., 95,* 68 (1951).

ENZYMATIC SACCHARIFICATION OF CELLULOSE BY THERMOPHILIC ACTINOMYCES

TAH-MUN SU and IRENE PAULAVICIUS

Physical Chemistry Laboratory,
Corporate Research and Development Center,
General Electric Company,
Schenectady, New York 12345

SYNOPSIS

Two strains of thermophilic actinomyces isolated in our laboratory were found to assimilate cellulosic fiber at a rate faster than that observed for *Trichoderma viride.* The actinomyces produced an extracellular enzyme which solubilized cellulose in the absence of cell mass. The specific enzyme production rate paralleled the specific growth rate of the culture. These findings prompted an examination of the thermophilic cell-free enzymatic saccharification of cellulosic fiber. The cell-free enzyme filtrate has a pH optimum of 5.5–6.5 and temperature optimum of 62°C. The kinetics of the enzymatic saccharification of pure cellulose and amorphous cellulose as a function of substrate concentration, enzyme concentration and particle size, were studied. The rate and extent of enzymatic saccharification of cellulosic fibers are limited by substrate crystallinity and enzyme inactivation. The crystallinity precluded adequate substrate accessibility, and prolonged incubation contributed to enzyme inactivation. Physical and chemical pretreatments for increasing substrate accessibility are effective but are presently too expensive to permit an economical process.

INTRODUCTION

The utilization of cellulose, the most abundant renewable organic resource, is one of the major challenges to technology. However, most of the cellulose is not in a form suited to human needs as food and fuel. The efficient utilization of cellulose by conversion to other useful materials would be simplified if the cellulose were hydrolyzed into soluble sugar, as shown in Figure 1. Complete hydrolysis of cellulose can be achieved in acid media at elevated temperatures. Unfortunately, the process has a low yield of glucose and produces undesirable by-products, such as acetic acid or furfural [1]. Cellulose can also be degraded by living organisms at a moderate temperature and pH [2]. The organisms produce extracellular enzymes (cellulase) that hydrolyze the cellulose into soluble sugar. The sugar is utilized for growth as shown on top of page 222.
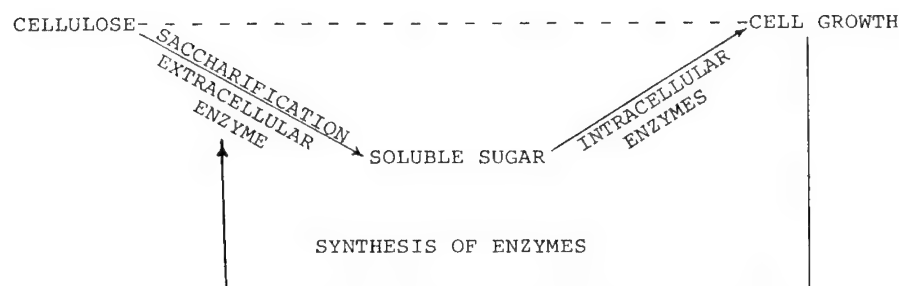
A process based on enzymatic saccharification might involve the use of isolated enzymes or the enzymes produced in situ by the organisms growing in the culture. The development of a practical enzymatic saccharification system requires (a) identification of an efficient microbial source of enzyme and (b) characterization of enzyme production and activity so as to define the optimum operating procedure.

A mesophilic fungus, *Trichoderma viride,* has received much attention in recent years as the major source of cellulase [3]. This microorganism is known to produce stable cellulase capable of effectively hydrolyzing treated cellulose fiber.

Our laboratory has been interested in the production of single-cell protein from cellulosic fiber by aerobic thermophilic microorganisms. Thermophilic conversion offers potential advantages of rate, pasteurization and temperature regulation over the mesophilic and anaerobic fermentations. Thermophilic actinomyces were found to digest the lignocellulosic fiber at a rapid rate [4]. Two of the strains of thermophilic actinomyces isolated by Bellamy were shown to have optimum growth at 55°C and pH 7.5–7.8 [4]. This paper will review the cellulase production and the factors that effect the rate of saccharification by the cellulase from one of the cultures, namely, MJϕr.

MATERIALS AND METHODS

Organism and Growth Media

The microorganism used in this study were two strains of thermophilic actinomyces MJϕr and YX, and a strain of fungus, *Trichoderma viride* QM9414. The
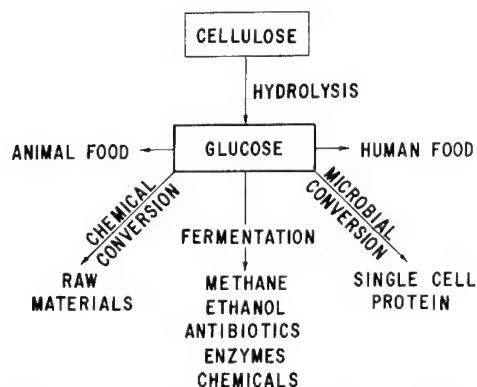
FIG. 1. Potential utilization of glucose produced from hydrolysis of cellulose.

thermophilic actinomyces MJ and YX were isolated by W. D. Bellamy. A mutant MJϕr, resistant to thermophilic actinophages was selected by A. M. Chakrabarty. *T. viride* QM9414, a second-generation mutant from the parent strain QM6a, was obtained from U.S. Army Natick Laboratory.

The composition of growth medium for MJϕr and YX was: $(NH_4)_2SO_4$ (5 g); K_2HPO_4 (10.44 g); KH_2PO_4 (5.4 g); NaCl (15 g); yeast extract (0.5 g); $MgSO_4 \cdot 7H_2O$ (0.2 g); $FeSO_4$ (20 mg); $MnSO_4 \cdot 4H_2O$ (20 mg); $CaCl_2$ (20 mg); $ZnSO_4$ (8 mg); Versenal (0.2 g); and 5 g of microcrystalline cellulose per liter of distilled water. The medium as recommended by Mandels and Weber was used for growing *T. viride* QM9414 [5].

Preparation of Cellulase

The enzyme used in this study was the cell-free culture filtrate without purification. MJϕr was grown in the medium containing 0.5% microcrystalline cellulose in the fermentor for 24–36 hr, after which the fermentation was stopped and harvested. The cell-free filtrate was obtained from a high-speed automatic regrigerated Sorval RC-2B centrifuge. The clear filtrate was preserved with 0.005% merthiolate. The filtrate contained 0.32 mg/ml of 5% trichloroacetic acid precipitable proteins. For some experiments, the cell-free filtrate was concentrated by ultrafiltration using PM10 (Amicon Co.) membrane in an Amicon thin-channel filtration system (Model TCT-10) at 4°C. The PM10 membrane has a nominal molecular weight cutoff at 10,000.

Substrates

Microcrystalline Cellulose. PH 105 Avicel was supplied by F.M.C. Corporation. The average particle size is 19μ. Less than 1% is retained on a 450 mesh screen. PH 102 Avicel has an average particle size of 90 μ.

Swollen Cellulose. PH 105 Avicel was dissolved in cold 85% H_3PO_4, precipitated with water and washed repeatedly with water as described by Walseth [6]. The cellulose was used directly without drying.

Analytical Methods

Soluble Sugar. Total soluble sugar was measured as glucose by the Anthrone method with glucose as a standard.

Undigested Cellulose. The undigested cellulose was dissolved in cold 72% H_2SO_4 and analyzed by the Anthrone method with glucose as a standard.

Protein. Protein was measured by the Lowry method with crystalline egg albumen as a standard. Cellular protein was prepared by sonicating the cell pellet in 0.1N NaOH solution for 3 min in an ice-water bath. The resulting clear supernatant from centrifugation was analyzed for cellular protein.

The soluble protein in the cell-free filtrate was precipitated overnight with 5% Trichloroacetic acid (TCA). The precipitant was redissolved in 0.1N NaOH solution for protein analysis.
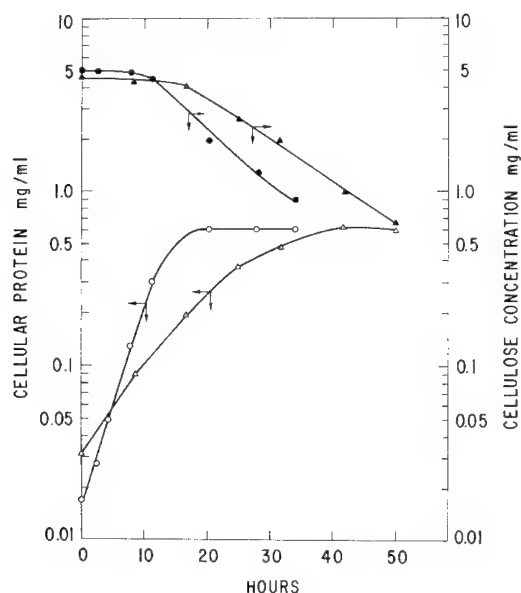
FIG. 2. Culture growth and substrate depletion by MJφr and *T. viride* in 0.5% microcrystalline cellu-lose. O — O: Growth of MJφr; ● — ●: cellulose depletion by MJφr; △ — △: growth of *T. viride;* ▲ — ▲: cellulose depletion by *T. viride.*

Cellulase Activity. The cellulase activity in this study was measured as mg/ml of glucose equivalents in the solution by incubating a mixture of one ml of enzyme solution and one ml of 20% microcrystalline cellulose (Avicel PH 105) in a pH 7.5 buffer solution at 55°C for 18 hr. The mixture was quenched by addition of 8 ml 0.1N H_2SO_4. The clear supernatant was analyzed for soluble sugar by the An-throne method.

EXPERIMENTS AND RESULTS

Growth of MJφr, YX and *T. viride* with Microcrystalline Cellulose

Figure 2 shows the relationship between the culture growth and substrate deple-tion by MJφr and *T. viride.* MJφr was grown in a 5-liter fermentor containing 0.5% microcrystalline cellulose (PH 105 Avicel) in a minimum basal medium at constant pH (7.5) and temperature (55°C). The fermentor was started with a 1%, 18-hr-old mycelial inoculum growing in shake flask, on the same medium as in the fermentor. Vegetative mycelium was used as inoculum to minimize the lag time.

T. viride was grown at constant pH (4.8) and temperature (28°C) in a basal medium [5] containing 0.5% Avicel. A vegetative mycelium was also used as in-oculum. The pH 4.8 was chosen for the fungus on the basis of an established pH optima for *T. viride* enzymatic saccharification of cellulose [7]. The culture growth was followed by the increase in cellular protein as measured by the Lowry method. The substrate depletion was followed by assaying the undigested cellu-lose.

<div align="center">TABLE I</div>
<div align="center">Specific Growth Rate and Cellulose Depletion Rate</div>

Culture	YX	MJϕr	T. viride
Specific Growth Rate hr^{-1}	0.32	0.26	0.1
Specific Cellulose Depletion Rate hr^{-1}	1.0	0.08	0.06

The cellulose depletion and the cell growth of thermophilic actinomyces were found to be faster than that of *T. viride*. It was interesting to note that the rate of the cellulose depletion was directly proportional to its concentration in the later stage of fermentation. The specific growth rate and the substrate depletion rate of the strains of thermophilic actinomyces and *T. viride* are shown in Table I.

Kinetics of Cellulase Production by MJϕr

Figure 3 shows the profiles of cellulase production by MJϕr during the growth in the fermentor. Since the cellulase can strongly adsorb on cellulose [8], it is necessary to analyze cellulase activity in both soluble and particulate fractions to account for all the cellulase produced by the microorganisms. Curve I represents the enzyme activity of the whole culture in the fermentor. Curve II describes the enzyme activity in the cell-free filtrate. Curve I shows that the total amount of the cellulase in the system roughly parallels the total cellular protein. Maximum
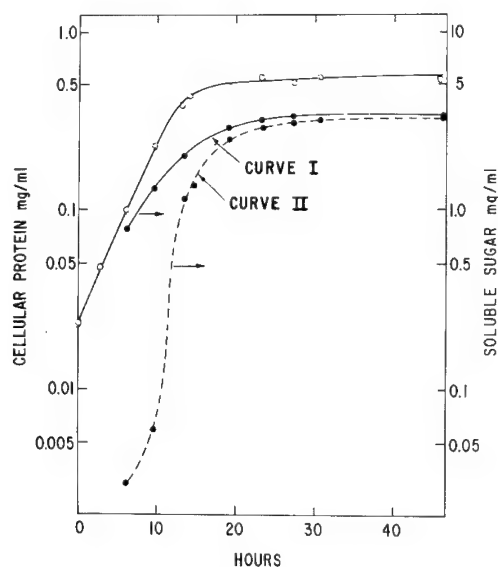
FIG. 3. Growth and cellulase production by MJϕr growing with 0.5% microcrystalline cellulose at 55°C and pH 7.5. O — O: cellular protein; ● — ●: total cellulase in the fermentor including cell mass, undigested cellulose and broth; ● - - - - - ●: Cellulase activity in cell-free filtrate.

TABLE II
Distribution of Cellulase Activity in Fermentor

Undigested Cellulose mg/ml	Cellulase Activity mg/ml Glucose Equivalent		
	Whole Culture	Particulate Fraction	Soluble Fraction
5.2	0.8	0.8	0.06
5.0	1.4	1.5	0.21
4.3	2.5	1.9	1.8
2.7	3.3	1.3	2.7
1.6	3.3	0.8	3.0

enzyme activity was obtained in stationary phase. No lag time was observed for the enzyme production. In contrast, considerable lag time was observed for the appearance of cellulase in the cell-free filtrate as shown in Curve II.

Distribution of the cellulase between the particulate and the soluble fractions in the fermentor is shown in Table II. The cellulase in the particulate fraction, containing undigested cellulose and cell mass, appeared first and gradually increased to a maximum value. It gradually declined, as the cellulose was further consumed by the microorganisms. A substantial cellulase activity in the soluble fraction was observed as the cellulase activity in the particulate fraction reached the maximum value.

Temperature and pH Optimum for Cellulase from MJϕr

Crude, cell-free filtrate was used in these experiments. The pH and temperature profiles are shown in Figures 4 and 5, respectively. To obtain the pH profiles, the enzyme activity was measured by incubating a mixture of 1.5 ml of 2% Avicel PH 105 in selected buffer solutions and 0.5 ml of cell-free filtrate at 55°C for 5 hr and 28 hr. The optimum pH was between 5.5 and 6.5. There was a suggestion of another maximum at higher pH. Temperature profile was measured at pH 6.0. The procedure was essentially the same as that described in the study of pH profile except that the incubation time was 3 hr. The optimum temperature was found to be 62°C.

Enzymatic Hydrolysis of Microcrystalline and Amorphous Celluloses

Figures 6 and 7 show the kinetic profiles of the saccharification of amorphous and microcrystalline celluloses by the cell-free filtrate from MJϕr as a function of the substrate concentration. The rate studies of hydrolysis were carried out by incubating a mixture of equal volumes of cell-free filtrate and the desired amount of the substrate at pH 6.0 and 65°C. A small sample was withdrawn from the mixture at timed intervals, and the amount of soluble sugar in the filtrate was determined.
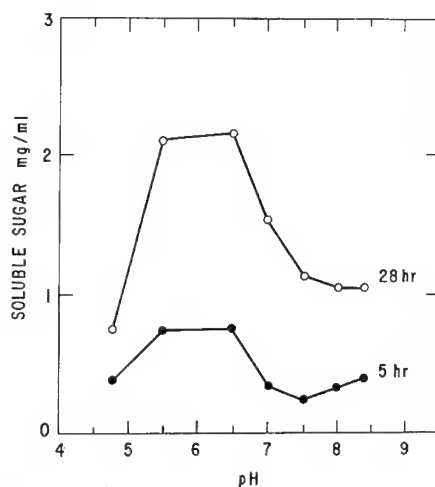
FIG. 4. pH profiles of cellulase activity from MJφr. Crude cell-free filtrate 0.5 ml and 2% Avicel pH 105 in 1.5 ml buffer solution in shaken test tube were incubated at 55°C. ● — ●: 5 hr of incubation; O — O: 28 hr of incubation.

Cell-free cellulase saccharified the amorphous cellulose effectively. The amorphous cellulose concentration below 3.4 mg/ml was completely hydrolyzed within 2 hr of incubation. However, as the amorphous cellulose concentration increased, the cellulase was less effective in hydrolyzing amorphous cellulose. Complete hydrolysis of 6.8 mg/ml amorphous cellulose required 24 hr of incubation while only 80% of the amorphous cellulose was saccharified at 10.1 mg/ml. Prolonged incubation did not increase the extent of the hydrolysis.

In contrast to the results observed in the saccharification of amorphous cellulose, cell-free filtrate was not able to hydrolyze the microcrystalline cellulose com-
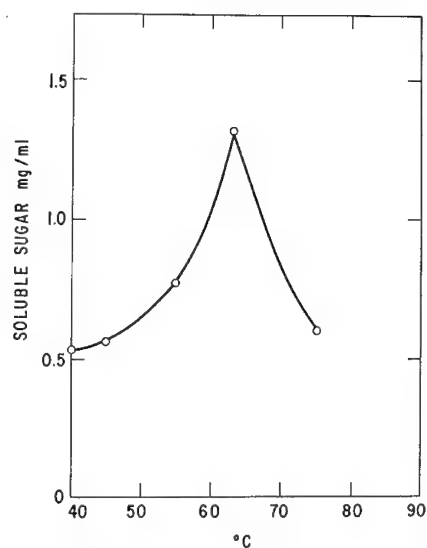
FIG. 5. Temperature profile of cellulase activity from MJφr. Crude cell-free filtrate 0.5 ml and 2% Avicel PH 105 in 1.5 ml buffer solution were incubated at pH 6.0 for 3 hr.
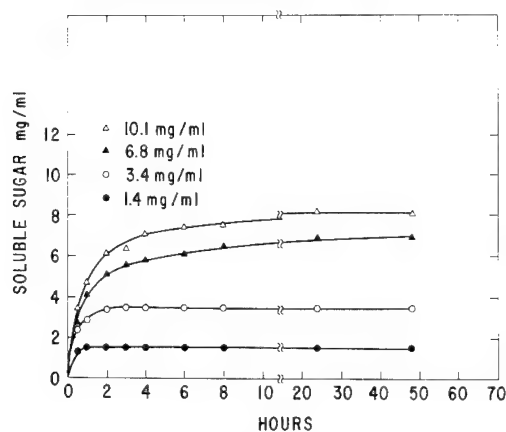
FIG. 6. Effect of substrate concentration on the saccharification of swollen cellulose by MJφr cellulase. The mixture of cell-free filtrate and the swollen cellulose was incubated at pH 6.0, 65°C.
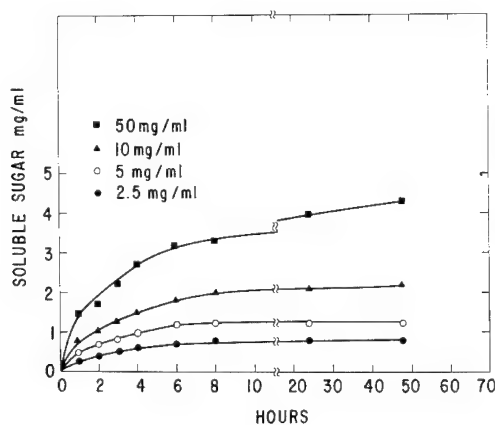
FIG. 7. Effect of substrate concentration on the saccharification of mirrocrystalline cellulose by MJφr cellulase. The conditions were as in Fig. 6.

pletely at 2.5 mg/ml. The extent of hydrolysis decreased as the substrate concentration increased as shown in Table III. At 2.5 mg/ml cellulose concentration, 32% of the Avicel was hydrolyzed during the first 8 hr of incubation and the remaining cellulose was resistant to hydrolysis. It appeared that about 30% of the

TABLE III

Degree of Saccharification of Microcrystalline Cellulose by MJφr Cellulase as Function of Substrate Concentration

Substrate Concentration	Percent of Saccharification	
mg/ml	8 Hr.	48 Hr.
2.5	32	32
5	25	25
10	20	22
50	6.6	8.6
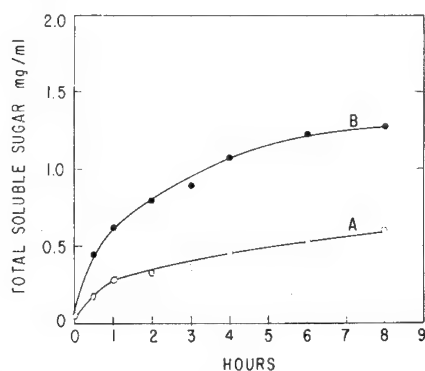
FIG. 8. Hydrolysis of partially hydrolyzed cellulose by MJφr cellulase. The conditions were as in Fig. 6. ● — ●: Curve B, control experiment, original microcrystalline cellulose; O — O: Curve A, partially hydrolyzed cellulose taken from Curve B after 48 hr of incubation.

microcrystalline cellulose was accessible for hydrolysis by the cell-free filtrate. At higher cellulose concentration, the cellulose was continuously, but slowly, saccharified following an initial rapid rate of hydrolysis.

Effect of Various Factors on the Saccharification Kinetics

In the study of the microcrystalline cellulose hydrolysis with cellulase, a marked decrease of the hydrolytic rate was observed despite the presence of excess substrate. At low substrate concentration, the enzyme can hydrolyze only about 30% of the microcrystalline cellulose and the remaining portion is resistant to further hydrolysis even after prolonged incubation. This observation is in contrast with that observed in the fermentor runs, where the microorganisms hydrolyze 90–95% of the microcrystalline cellulose within 48 hr. Factors which are considered to be possible causes of the declining enzymatic hydrolytic rate are: 1) a decrease of the accessibility of the cellulose resulting from the removal of its more accessible portions, 2) inactivation of the cellulase by heat, and 3) inhibition of the enzyme activity by the accumulated reaction products. The following experiments were carried out to evaluate the relative effect of these factors on the hydrolytic rate of the cellulose.

Hydrolysis of Partially Hydrolyzed Microcrystalline Cellulose. Microcrystalline cellulose (5 mg/ml) was treated with the enzyme for 48 hr. The residual cellulose was separated from the hydrolyzate and washed with water. Then it was further treated with the same amount of the fresh enzyme as that used with the original microcrystalline cellulose. This partially hydrolyzed cellulose was further hydrolyzed by the fresh enzyme, but the hydrolytic rate was lower than that found in the original substrate, as shown in Curves A and B in Figure 8. The lower initial rate in Curve A is likely due to the accumulation of crystalline cellulose.

Thermal Stability of Cellulase in Cell-Free Filtrate. The thermal stability of the cell-free cellulase was studied at 50 and 60°C at constant pH (7.5). The filtrate was incubated in the constant temperature bath for 8 and 24 hr. The cellulase activity in the heat-treated cell-free filtrate was measured by incubating the cell-free filtrate containing 100 mg/ml of microcrystalline cellulose at 55°C and
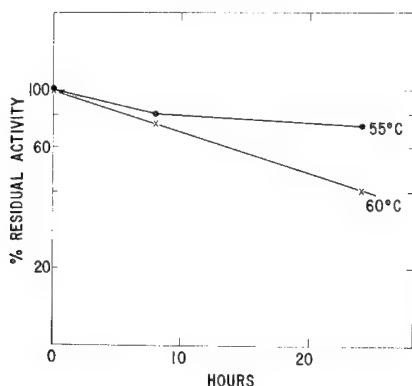
FIG. 9. Thermal inactivation of MJϕr cellulase. Cellulase Activity: Cell-free filtrate containing 100 mg/ml Avicel PH 105 was incubated at pH 7.5, 55°C.

pH 7.5 for 3 hr. As shown in Figure 9, the cellulase is relatively unstable at its optimum temperature (60°C) and exhibits a first-order decay with a half-life of 24 hr. At 55°C the enzyme is relatively stable. The enzyme loses about 20% of its original activity in the first 8 hr and only 7% in the following 16 hr.

Inhibition of Cellulase Activity by Glucose and Cellobiose. A mixture of 50 mg/ml of microcrystalline cellulose and cell-free filtrate containing desired amounts of glucose or cellobiose was incubated for 3 hr, and the total soluble sugar was measured. The concentration of the glucose and the cellobiose was varied from 0.25 mg/ml to 5 mg/ml. Glucose and cellobiose concentrations higher than 5 mg/ml were not studied because the total soluble sugar produced in the control experiment did not exceed 3 mg/ml. At a concentration of 5 mg/ml, the glucose or cellobiose caused only 10% inhibition.

Repeated Treatment of Cellulose with Fresh Enzyme

In the hydrolysis of swollen and microcrystalline celluloses at high substrate concentration, the initial rate of hydrolysis gradually decreased after 3 hr of incubation, despite the presence of a large excess of substrate. It was found that the initial rapid rate of hydrolysis could be maintained when the cell-free fresh enzyme was repeatedly introduced into the partially hydrolyzed swollen cellulose, as is shown in Figure 10. The swollen cellulose in the cell-free filtrate was incubated at 65°C in a buffer solution (pH 7.5) and the supernatant was removed at 3-hr intervals, as shown by the arrow. The residual cellulose was washed once with distilled water and then incubated again with the same amount of fresh enzyme. Similar results were also observed with 10% and 2% microcrystalline cellulose, as is shown in Figure 11.

Effect of Particle Size on the Enzymatic Saccharification of Microcrystalline Cellulose

Hydrolysis of two different particle sizes of microcrystalline cellulose was studied. The results are shown in Figure 12. Avicel PH 102 and PH 105 have a me-
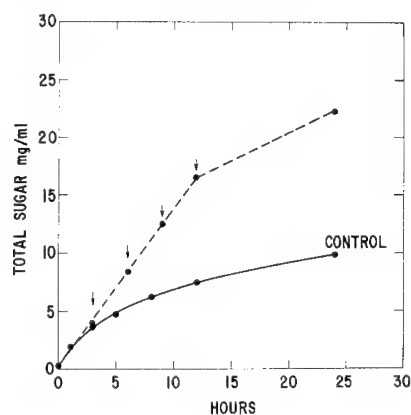
FIG. 10. Saccharification of H_3PO_4-treated microcrystalline cellulose with addition of fresh MJφr cellulase. Swollen cellulose, 44 mg/ml, in cell-free filtrate was incubated at pH 7.5, 65°C. ● — ●: Control experiment, without replenishing the fresh enzyme; ● - - - - ●: Addition of fresh enzyme after the hydrolyzate was removed and the residue was washed with water.

dian diameter of 85.5 and 16.5 μm, respectively [9]. Only a 25% increase in the initial hydrolytic rate was observed by reducing the particle size fivefold.

Effect of Enzyme Concentration on the Saccharification of Microcrystalline Cellulose

Figure 13 shows the saccharification kinetics of microcrystalline cellulose at different concentrations of the cellulase. The cell-free filtrate concentration was in-
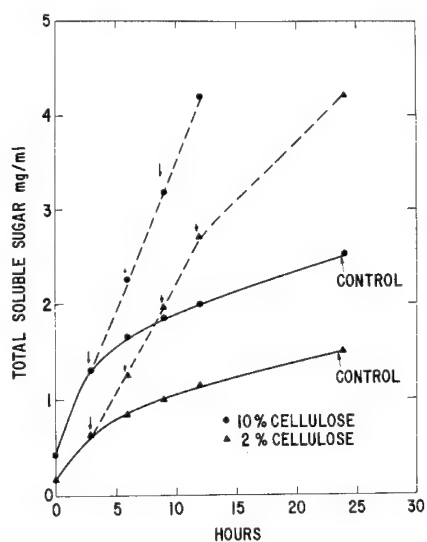
FIG. 11. Saccharification of microcrystalline cellulose with addition of fresh MJφr cellulase. The conditions were as in Fig. 10. ▲ — ▲ and ● — ●: Control experiments, 2% and 10% microcrystalline cellulose, respectively; ▲ - - - - ▲ and ● - - - - ●: Addition of fresh cell-free filtrate after the hydrolyzate was removed and the residue was washed with water; 2% and 10% microcrystalline cellulose, respectively.
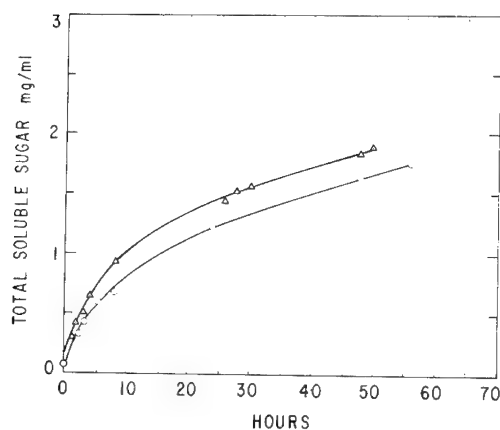
FIG. 12. Effect of particle size on the rate of soluble sugar production by MJϕr cellulase. Substrate 5 mg/ml in cell-free filtrate was incubated at pH 7.5, 55°C. Δ — Δ: PH 105 Avicel, median diameter 16.5 μm; O — O: PH 102 AVICEL, median diameter 85.5 μm.

creased 10-fold in a cold room (4°C) by thin-channel membrane filtration. TCA precipitable protein in the final solution was 4.4 mg/ml as compared to 0.4 mg/ml in the original cell-free filtrate. The concentrated enzyme solution was diluted with buffer solution to the desired concentration, and the enzyme solution was incubated with microcrystalline cellulose (100 mg/ml) at 55°C and pH 7.5. The rate and the extent of the hydrolysis of the cellulose increased as the enzyme concentration increased. The amount of increase was not proportional to the increase in the enzyme concentration. The tenfold increase in the cellulase concentration only increased the rate and extent of the saccharification by a factor of 2.3 in 8 hr of incubation.

DISCUSSION

Results of comparative study of culture growth and substrate consumption by two strains of thermophilic actinomyces and *T. viride* (Fig. 1 and Table I) suggest that either the activity of the cellulase from thermophilic actinomyces or the rate
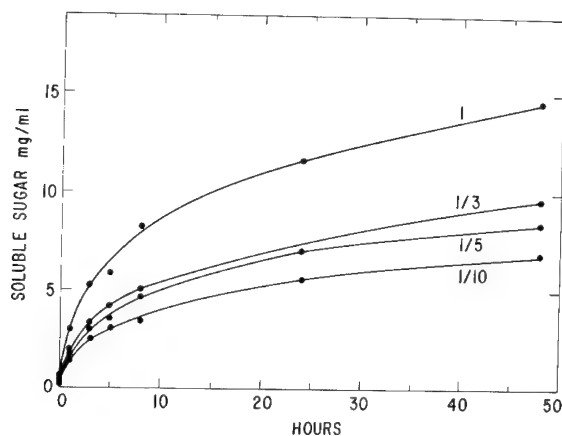
FIG. 13. Effect of enzyme concentration on the soluble sugar production by MJϕr cellulase. Microcrystalline cellulose 100 mg/ml in desired enzyme concentration was incubated at pH 7.5, 55°C.

of cellulase production or both are superior to that of *T. viride* under the fermentation conditions.

The production of cellulase by MJϕr parallels the culture growth. The cellulase activity reaches a maximum value at the stationary phase of culture growth. Since the cellulase activity in the cell-free filtrate has the same activity as that found in the culture broth containing the microorganisms, the cellulase produced by MJϕr is an extracellular enzyme and is not associated with the microorganisms. Consequently, the cellulase can be harvested in the cell-free filtrate and be used directly.

Although the cellulase produced by the microorganisms was found to parallel the culture growth, a considerable lag time was observed before the cellulase appeared in the filtrate (Fig. 3, Curve II). Distribution of the cellulase activity in particulate and cell-free filtrate fractions (Table I) suggests that the lag time is due to adsorption of the cellulase on the cellulose. The small amount of cellulase produced by the microorganisms at the early stage of fermentation is mostly adsorbed on the cellulose. As the fermentation proceeds, the microorganisms produce more enzyme which begins to appear in the filtrate as the surface of the cellulose becomes saturated with the enzyme.

Cellulase activity produced by MJϕr was evaluated with microcrystalline and swollen celluloses because these two substrates represent the two morphological extremes in cellulosic fibers. The microcrystalline cellulose contains 86% crystalline cellulose based on x-ray analysis; this degree of crystallinity is comparable to that in native cotton [10]. It is relatively resistant to dilute acid [11] and enzymatic hydrolysis [6]. The advantages of using the microcrystalline cellulose over cotton are: 1) easier to handle at high substrate concentration, 2) higher surface area (0.24 m^2/g for Avicel PH 105) [9], and 3) available commercially at various particle sizes. The swollen cellulose obtained by treating the microcrystalline cellulose with cold 85% H_3PO_4 is essentially an amorphous cellulose and is readily accessible to cellulase [12]. Never-dried swollen cellulose was used in this study because the porosity and the accessibility of the swollen cellulose tend to decrease during the process of drying [12].

As is shown in Figure 4, cellulase from MJϕr effectively hydrolyzes the swollen cellulose in a very short period of incubation. On the other hand, the enzyme is much less reactive toward the solubilization of the microcrystalline cellulose (Fig. 5). The initial hydrolytic rate of the swollen cellulose is much faster than that of the microcrystalline cellulose at comparable substrate to enzyme ratios. A similar observation was also reported with other enzyme systems [6,13]. This difference in the rate of hydrolysis between the swollen cellulose and the microcrystalline cellulose is attributable to the difference in the porosity and the accessibility [12]. Stone found that the initial enzymatic hydrolytic rate of cellulose is proportional to fiber saturation point and median pore size [12]. The fiber saturation point, defined as the amount of water inaccessible to a very large molecule (molecular diameter 1600 Å), increases from 0.48 ml/g for cotton treated with water alone to 1.4 ml/g for cotton swollen in 78.8% H_3PO_4. The corresponding median pore size increases from 32 Å to 52 Å. This large pore size enhances cellulase penetration into the cellulose. Since similar increases in the pore size and the water saturation point can be expected in the swollen cellulose obtained by treating the microcrystalline cellulose with phosphoric acid, the swollen cellulose will be hydrolyzed much faster than the microcrystalline cellulose.

The observed incomplete hydrolysis of the microcrystalline cellulose by the cell-free enzyme (Fig. 5, Table II) is in contrast to that seen in the fermentor where the microorganisms completely utilize the cellulose in two or three days (Fig. 1). The degree of saccharification depends on the substrate concentration. For substrate concentrations of 5%, the hydrolysis of the cellulose consists of a fast initial hydrolytic reaction followed by a slower one. At the end of 48 hr of incubation, only 8.6% of the cellulose is solubilized. Although the cellulase is able to hydrolyze 30% of a 0.25% cellulose suspension, prolonged incubation does not increase the degree of saccharification. The decrease in the rate of hydrolysis can be caused by either the limited substrate availability or inactivation of the enzyme, or both. The results obtained from the hydrolysis of partially hydrolyzed cellulose with fresh enzyme (Figs. 6–8) suggest that the decrease in the substrate accessibility alone cannot satisfactorily account for the incomplete hydrolysis of microcrystalline cellulose. In Figure 6, the lower initial hydrolytic rate observed in Curve A as compared with the original substrate in Curve B is due to the decrease in accessibility of the residual cellulose. However, since the addition of fresh enzyme to the partially hydrolyzed cellulose can maintain the initial fast rate of hydrolysis, as shown in Figures 7 and 8, the inactivation of the cellulase is probably the primary cause of the decrease in hydrolytic rate.

Products from hydrolysis and thermal denaturation of enzyme can inactivate the enzyme activity. With MJϕr cellulase, product inhibition becomes significant only in the presence of high product concentration as observed in the *T. viride* enzyme system [7]. The cellulase activity from MJϕr decreases by only 10% at 5 mg/ml of glucose or cellobiose. Since the decrease of hydrolytic rate occurs at a very low soluble sugar concentration (below 3 mg/ml), product inhibition is not likely to be the major factor causing inactivation of the enzyme. This assessment leads one to deduce that the progressive denaturation of the cellulase is the principal cause for the incomplete hydrolysis of the microcrystalline cellulose. The cellulase is relatively unstable at its optimum temperature (Fig. 9). The half-life at 60°C is 24 hr. The existence of two slopes in the enzyme inactivation at 55°C indicates that the cellulase activity of MJϕr is probably dependent on two or more enzymes, differing in thermal stability, as observed in the enzymes from *T. viride* [14]. Therefore, the discrepancy between the extent of the microcrystalline cellulose solubilization in the fermentor and the cell-free enzyme can be accounted for by the continuous resupply the fresh enzyme which occurs during fermentation.

Insensitivity of the hydrolytic rate or degree of saccharification of the microcrystalline cellulose with a fivefold reduction in particle size is contrary to expectation (Fig. 12). Since cellulose saccharification is a heterogeneous catalytic reaction, one would expect that the rate of hydrolysis would be proportional to the surface area in contact with the solute. The cellulase from *T. viride* is also reported to be insensitive to the particle size [8]. These results can be best interpreted by the equation developed by McLaren describing the hydrolytic rate of enzymatic reaction in a heterogeneous system [15]. He treated enzyme adsorption by considering the enzyme to be a solute, partitioning between a liquid phase and a solid phase. Assuming that the adsorption can be described by the Gyani-Freundlich isotherm and all the adsorbed enzyme is involved in "productive binding," the rate of hydrolysis is proportional to the exponential function of enzyme concentration as shown below:

$$V = K[E]^n$$

where V is the rate of hydrolysis, K is constant, and [E] is the enzyme concentration. The value of n describes the adsorption characteristic of the enzyme on the surface of the substrate. Adsorption on cracks or edges gives $n = \frac{1}{3}$ and adsorption on surface gives $n = \frac{2}{3}$. The value of n can be easily obtained from the study of hydrolytic rate at different enzyme concentrations. Based on the results obtained in Figure 13, the n value in MJϕr enzyme system is 0.35. It indicates that the adsorption of the cellulose occurs on the crack edge of the microcrystalline cellulose. A similar low value of n (0.48) was also observed for *T. viride* enzyme on the microcrystalline cellulose [16]. It appears that the hydrolysis of the microcrystalline cellulose takes place primarily on the crack edges of the surface of the particle. This observation might explain the results obtained in Figure 12.

CONCLUSION

From these experiments, we have learned that the thermophilic actinomyces strans MJϕr and YX grow and degrade the microcrystalline cellulose faster than *T. viride*. The cellulase production of MJϕr roughly parallels the cellular protein, and the cellulase activity reaches maximum activity in the stationary phase. There is a lag time in the appearance of cellulase in the filtrate. The lag time is due to the strong adsorption of the cellulase on the undigested cellulose. The optimum pH and temperature of the cellulase are near the optimum conditions for the growth of MJϕr. The enzyme hydrolyzes swollen cellulose effectively. However, the enzyme can hydrolyze only 30% of the microcrystalline cellulose. This is due to the gradual thermal deterioration of the enzyme during the saccharification. The cell-free enzyme is relatively stable at 55°C, but a first-order decay with a half-life of 24 hr is observed at 60°C. There are two slopes of decay at 55°C which indicate that the cellulase activity of MJϕr is dependent upon enzymes differing in thermal stability.

We conclude on the basis of our study, that MJϕr is a significant potential source of cellulase for use in the enzymatic saccharification processes. However, the problem of enzyme inactivation will remain a barrier to economic utilization until future research provides the means to minimize loss of activity.

REFERENCES

[1] W. Faith, *Ind. Eng. Chem.*, *37*, 9 (1945).

[2] J. Gascoigne and M. Gascoigne, *Biological Degradation of Cellulose,* Butterworth, London, 1960.

[3] M. Mandels, in *Cellulose as a Chemical and Energy Resource* (*Biotechnology Bioengineering Symp.* No. 5), C. R. Wilkie, Ed., Wiley-Interscience, New York, 1975, p. 81.

[4] W. D. Bellamy, *Biotech. Bioeng.*, *16*, 869 (1974).

[5] M. Mandels and J. Weber, "Cellulase and Their Application," American Chemical Society, *Advances in Chemistry Series*, 1969, p. 391.

[6] C. Walseth, *TAPPI*, *35*, 228 (1952).

[7] T. Ghose, *Biotech. Bioeng.*, *11*, 239 (1969).

[8] M. Mandels, J. Kostick, and R. Parizek, *J. Polym. Sci. C*, *No. 36*, 445 (1971).

[9] K. Marshall and D. Sixsmith, *Drug Development Communication*, *1* (1), 51 (1974).

[10] K. Ogura and H. Sobue, *J. Appl. Polym. Sci., 14,* 1390 (1970).

[11] A. Meller, *J. Polym. Sci., 9,* 619 (1949).

[12] J. Stone, A. Scallan, E. Donefer and E. Ahlgren, "Digestibility as a Simple Function of a Molecule of Similar Size to a Cellulase Enzyme," American Chemical Society, *Advances in Chemistry Series,* 1969, p. 219.

[13] A. Huang, U.S. Army Natick Laboratory, private communication.

[14] T. Su and I. Paulavicius, *Appl. Microbiol.,* in press.

[15] A. McLaren, *Enzymologia, 26,* 237 (1963).

[16] T. Su and I. Paulavicius, unpublished results.

LIQUID CHROMATOGRAPHY FOR MONITORING THE CONVERSION OF CELLULOSIC WASTES TO SUGARS

JAMES K. PALMER*

*Food Sciences Laboratories,
U.S. Army Natick Development Center,
Natick, Massachusetts 01760*

SYNOPSIS

High-performance liquid chromatography has been applied to the analysis of the sugars produced during the enzymatic hydrolysis of cellulosic wastes. The three primary products—xylose, glucose and cellobiose—can be separated in 4 min, and microgram quantities can be determined with good precision and accuracy. Filtration is the only pretreatment required. Minor sugars which are commonly present in the hydrolysates can also be separated for analysis or identification by modifications in the eluting solvent. Use of the method is illustrated with samples from a study of the effect of temperature (45–60°C) on the hydrolysis of ball-milled newspaper by an enzyme preparation from *Trichoderma viride*. Temperature had little effect on the extent of saccharification, but markedly affected the rate of saccharification and the relative concentration of glucose and cellobiose in the hydrolysates.

INTRODUCTION

Mandels and colleagues [1,2] have provided extensive documentation concerning the conversion of cellulosic wastes to sugars by cellulase preparations from selected strains of *Trichoderma viride*. In these studies, the rate and extent of saccharification were followed by measuring reducing sugar by a dinitrosalicylic acid procedure as glucose in the hydrolysates, although it was recognized that the hydrolysates normally contained a mixture of xylose, glucose and cellobiose [2].

As the system becomes more refined and closer to the point of actual application to produce sugars, it is necessary to obtain data on the actual quantities of xylose, glucose and cellobiose in the reaction mixtures. This will hopefully make it possible to optimize conditions for production of glucose. Also, there could be significant quantities of other sugars present, some perhaps worth recovering, or others which might affect the potential usefulness of the sugar syrups for chemical feedstocks, single-cell protein production, etc.

The general application of high-performance liquid chromatography (LC) to sugar analyses is described by Palmer [3]. This report provides details on the application of LC to analysis of cellulose hydrolysates, with special reference to newspaper hydrolysates.

---

* Present Address: Department of Food Science and Technology, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.

Another report in this symposium volume [4] describes the application of the LC methods to studying the susceptibility of various cellulosic wastes to enzymic hydrolysis (relative to newspaper).

MATERIALS AND METHODS

Sugar Standards

Xylose, glucose and cellobiose were of the highest purity obtainable from Nutritional Biochemicals Co. Concentrated stock solutions were prepared and concentrations determined by polarimetry. Working standards in the range of 1–20 mg/ml (0.1–2%) were prepared by dilution. Gentiobiose was obtained from Aldrich Chemical Co. Laminaribiose, cellotriose and higher oligomers were kindly supplied by E. T. Reese.

High-Performance Liquid Chromatography

Waters Associates ALC-100,* equipped with Model 6000 Solvent Delivery System; differential refractometer detector, sensitivity 1×10^{-7} refractive index units, attenuation 64 to $\frac{1}{4}$; Texas Instruments Servoriter II, 10 mV full scale, variable chart speed (usually 0.2–0.75 in./min); columns, Waters Associates "μBONDAPAK/Carbohydrate," 30 cm $\times$ 4 mm ID stainless steel; column temperature, 25°C; eluent, water:acetonitrile mixtures, filtered through 3 μ Millipore filter before use; flow rate, 1–5 ml/min at pressures up to 3500 psi. Samples (usually 20 μl) were injected with a syringe (Precision Sampling Corporation) through a septum or via the Waters Associates Model U6K Universal Injector.

The concentrations of xylose, glucose, cellobiose in hydrolysates were determined from peak-height measurements, relative to peak-height standard curves prepared with authentic sugars. The concentrations in minor unidentified peaks were approximated from the peak heights, relative to the standard curve for the known sugar with the closest retention time.

Paper Chromatography

Sugars were spotted on Whatman No. 1 paper and developed overnight (descending) with isopropyl alcohol:glacial acetic acid:water, 54:8:18 [5]. Sugars were located by spraying with 1% p-anisidine hydrochloride in ethanol, followed by brief heating at 100°C [6].

Reducing Sugar and Total Sugar

Reducing sugar was measured as glucose by a dinitrosalicylic acid (DNS) method [7], and total sugar by the phenol–sulfuric acid method [8].

* Reference to trade names is for information only and does not constitute endorsement by the U.S. Army.

Enzymic Hydrolysis (Saccharification)

The purified cellulose was Solka Floc BW 200, a 200-mesh, ball-milled pulp prepared from Solka Floc SW 40 (Brown Co., Berlin, N.H.). A 200-g sample of BW 200 was slurried in a solution containing 50 ml of 1M citrate, pH 4.8; 250 ml of water, and 500 ml of a concentrated cellulase preparation from *Trichoderma viride* QM 9414 to give 20% BW 200 and 2 Filter Paper cellulase units (2 mg of protein) per ml in the reactor [4]. Hydrolysis was carried out in a stirred (200 rpm) tank reactor at 50°C. Samples were taken at selected times and centrifuged to remove particulates. Samples of the supernatant fluid were withdrawn for reducing sugar analysis via the DNS method, and the remainder was frozen. Immediately prior to analysis by LC, the samples were thawed, mixed thoroughly and filtered through a 3 μ Millipore filter. (Recent studies indicate that a 0.45 μ filter is preferable, to prevent possible clogging of column end fittings.) Aliquots of the filtrate were taken for analysis by LC and for reanalysis via the DNS method. In all cases, the repeat DNS values were the same as the earlier analyses within the limits of experimental error. Since 1 mg of cellulose gives 1.1 mg of glucose, percent saccharification for this 20% slurry equalled mg/ml glucose (via DNS) $\times$ 0.45.

The newspaper (Sweco NP) used was The Boston Globe, milled in a Sweco mill as described earlier [2]. Saccharification and sugar analysis were carried out essentially as with purified cellulose, except that 200 g of Sweco NP was slurried in a reaction mixture containing 50 ml 1M citrate, pH 4.8, and 950 ml of cellulase concentrate to give 16.7% Sweco NP and 2.0 Filter Paper units per ml in the reactor. The hydrolyses were carried out at 45, 50, 55 and 60°C. Percent saccharification in these runs was calculated as mg/ml total LC sugars (as glucose) $\times$ 0.60.

EXPERIMENTAL AND RESULTS

Analysis of Hydrolysates of Purified Cellulose

Enzymatic hydrolysates of Solka-Floc BW 200 were first analyzed as a guide to interpreting results from the hydrolysis of cruder cellulosic wastes such as newspaper. Figure 1 is a typical chromatogram, confirming an earlier report [2] that xylose, glucose and cellobiose are the three primary products when this purified cellulose is hydrolyzed by *T. viride*. The hydrolysate of Figure 1 contains 4.9 mg/ml xylose, 32.4 mg/ml glucose and 18.0 mg/ml cellobiose. No higher oligomers were detected when samples were analyzed under conditions (35% water in the eluent) where these oligomers were readily separated [3]. The hydrolysates required no pretreatment except filtration through a Millipore filter. Thus, the total time per sample for preparation and analysis was no more than 10 min.

The quantitative aspects were explored for xylose, glucose and cellobiose. Standard curves (based on peak heights) prepared with aqueous solutions of pure sugars were linear over the range tested (20–400 μg individual sugar injected), when the total volume injected did not exceed about 100 μl. The slopes of the peak-height standard curves (i.e., the peak height/μg injected) were different for each sugar. The slopes of the standard curves also varied with volume injected, being 8–10% less at 100 or 200 μl injected than at 5–40 μl injected. Based on in-
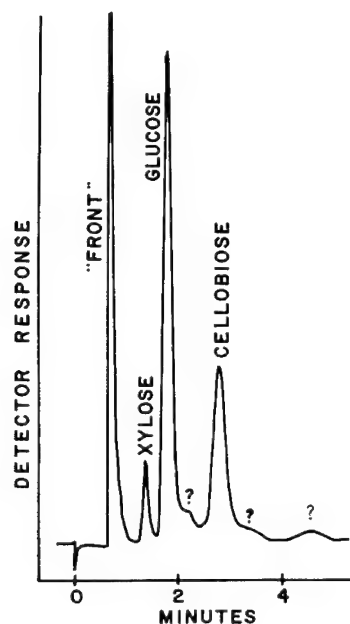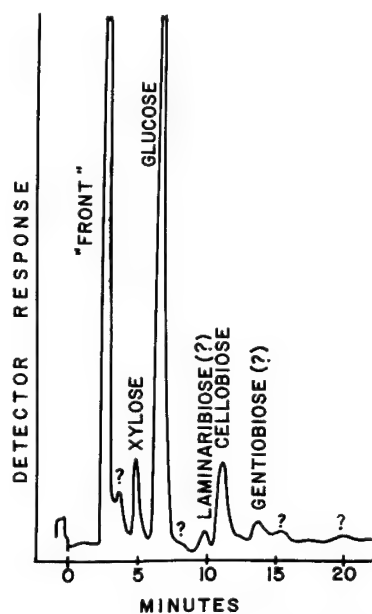
FIG. 1. Separation of sugars in a hydrolysate of purified cellulose. Sample, 20 μl. taken after 13 hr hydrolysis; eluent, water:acetonitrile, 25:75; flow rate, 5.0 ml/min; attenuation, ×8; chart speed, 0.75 in./min.

jecting 200 μl containing 20 μg of sugar, xylose and glucose concentrations of 0.1 mg/ml (0.01%) could be routinely analyzed and considerably lower concentrations could be detected. The corresponding limit for cellobiose was 0.2 mg/ml. Since the hydrolysates rarely contained less than 1 mg/ml of any sugar and always contained appreciably higher concentrations of glucose and cellobiose, 20 μl was normally injected, thus avoiding possible effects due to sample volume. The precision and accuracy of the method for these three sugars was determined with newspaper hydrolysates and is discussed later.

Chromatograms run under the conditions of Figure 1 indicated the presence of 3 minor sugar components. Increased resolution of the minor sugars was obtained by lowering the water content of the eluent to 20%. These chromatograms (Fig. 2) indicated the presence of 5 minor sugars. The increased resolution made it possible to measure the retention times of the sugars more precisely relative to authentic sugars and also made it possible to inject up to 100 μl samples of the relatively concentrated hydrolysate (about 6% total sugars) and still obtain essentially the same separation as in Figure 2. Multiple injections were made and samples representing each of the peaks were collected and analyzed by paper chromatography. In this way, the identities of xylose, glucose and cellobiose were confirmed and two of the minor components were tentatively identified as laminaribiose and gentiobiose (Fig. 2). Based on retention time versus an authentic standard, cellotriose was earlier [3] identified as the sugar responsible for the last peak of Figure 2. Paper chromatography revealed that it was not cellotriose. Studies on the identity of this and the other minor sugars are continuing.

It is possible that some cellulosic wastes will contain minor quantities of other cell wall-derived monosaccharides, such as rhamnose, mannose, or galactose. With 25% water in the eluent (Fig. 1), rhamnose would not separate from xylose;

FIG. 2. Increased resolution of minor sugars in a hydrolysate of purified cellulose. Sample 20 μl. taken after 24 hr hydrolysis; eluent, water:acetonitrile, 20:80; flow rate, 1.5 ml/min; attenuation, ×8; chart speed, 0.2 in./min.

mannose and galactose would not separate from glucose. However, all these monosaccharides can be separated by reducing the water content in the eluent to about 15% [3]. The BW 200 hydrolysates contained no measurable quantities of these sugars, as determined by LC and by paper chromatography of the collected glucose and xylose fractions.

Figure 3 shows typical data on the accumulation of sugars during the enzymatic hydrolysis of purified cellulose. The characteristic features were:
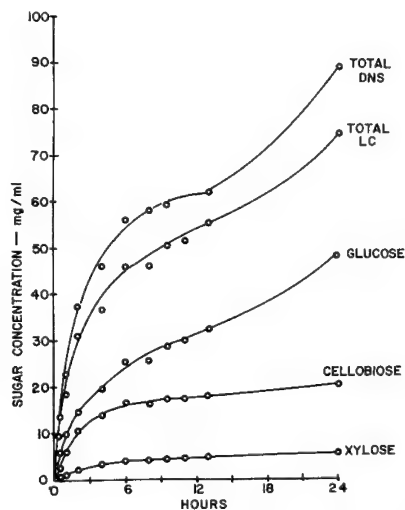
FIG. 3. Accumulation of sugars during enzymatic hydrolysis of purified cellulose. See text for experimental details.

1. Xylose, glucose and cellobiose accounted for 90% or more of the "total LC" sugars.

2. Xylose accumulated slowly and represented only a fraction (7% in Fig. 3) of the "total LC" sugars after 24 hr hydrolysis.

3. Cellobiose accumulated rapidly for the first few hours, but only slowly after that. In some other experiments, with different grades of purified cellulose, the cellobiose concentration actually fell significantly in the later stages of hydrolysis. The level of cellobiose present at any time is a reflection of its rate of production by cellulase and its rate of decomposition by β-glucosidase.

4. Glucose accumulated rapidly at first and continued to accumulate at a relatively rapid rate throughout.

5. The ratio of glucose:cellobiose at 24 hr was about 2.5:1.

The actual kinetics of hydrolysis and the total saccharification achieved (40% in the run of Fig. 3, based on total reducing sugars via the DNS method) vary considerably depending on the nature and pretreatment of the cellulose, and the concentration of substrate and enzyme used [2,4].

Since xylose, glucose and cellobiose account for more than 90% of the sugars in hydrolysates of most cellulosic wastes [4], "total LC" sugars (shown in Fig. 3) refers to the sum of these three sugars. When the approximate concentration of the minor sugars of Figure 1 was added to the "total LC" sugars, the sum was identical, within experimental error, with "total DNS" sugars.

Analysis of Newspaper Hydrolysates

Chromatograms of newspaper (NP) hydrolysates, run under the conditions given in Figure 1, proved to be similar to those for purified cellulose. The only variation noted was in the number and retention times of peaks representing minor components. This has been the general pattern for a variety of cellulosic wastes [4]. The precision (coefficient of variation) for repeated analyses of several NP hydrolysates under these conditions was 1–2% for glucose and cellobiose and about 3% for xylose. To test accuracy, two different NP hydrolysates (from the 45°C series described below) were mixed 1:1 with a standard solution of the three sugars, so that the final concentration of each sugar in the mixture approximated the concentration in the original NP hydrolysates. Recovery (mean ± standard deviation) of the added glucose and cellobiose was 101 ± 1.3%, of xylose, it was 100 ± 6.5%.

As with the purified cellulose, the only pretreatment required for NP hydrolysates was filtration through a 3μ filter. The total preparation and analysis time for the three primary sugars was about 10 min.

Effect of Temperature on Enzymatic Hydrolysis of Newspaper (NP)

A temperature of 50°C has generally been used in these laboratories to screen cellulosic wastes for susceptibility to enzymic hydrolysis [2]. The experiments in this report provided data on the effect of temperature on the rate and extent of saccharification of ball-milled NP, and on the proportions of xylose, glucose and cellobiose in the reaction mixture.
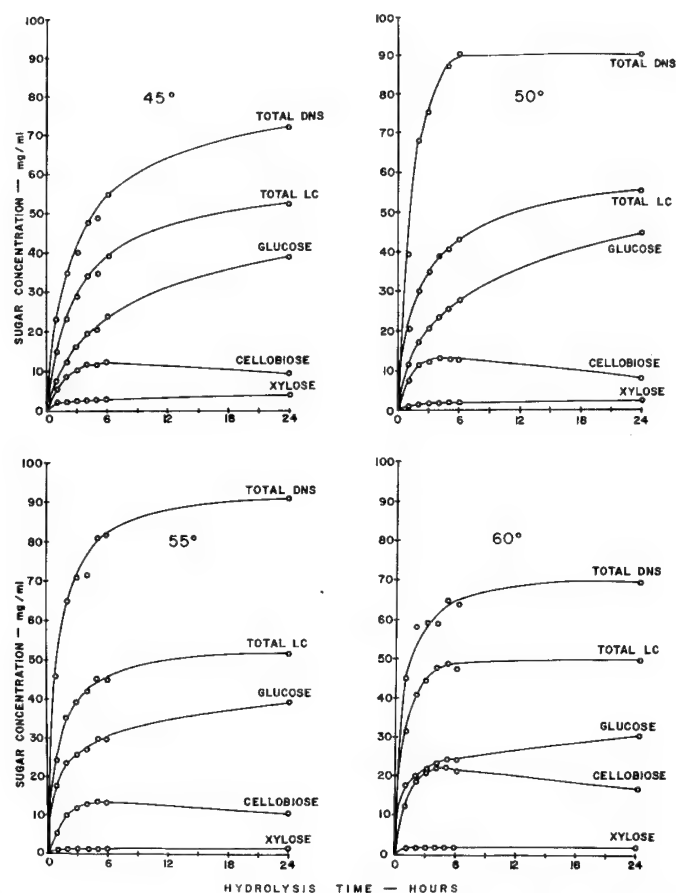
FIG. 4. Effect of temperature on the accumulation of sugars during enzymatic hydrolysis of newspaper. See text for experimental details.

Figure 4 shows the time course of hydrolysis of NP at temperatures from 45 to 60°C. The overall pattern of hydrolysis is comparable to that for pure cellulose (Fig. 3), and the saccharification achieved at all temperatures was about 31% (Table I), based on "total LC" sugars. However, the rate of saccharification increased noticeably, and the glucose:cellobiose ratio decreased noticeably at temperatures exceeding 50°C (Table I).

TABLE I
Saccharification of Newspaper at Various Temperatures

Temp. °C	Saccharification %	Rate of Saccharification -hrs. to reach 90% of 24 hr. value	Ratio of Glucose to Cellobiose at 90% point	Glucose as % of total LC sugars at 90% point
45	32	13	3.0	69
50	33	13	3.3	75
55	31	7	2.4	67
60	30	3	1.0	48

With the NP samples, there has consistently been a significant and variable discrepancy between the "total LC" sugars and the "total DNS" sugars (Fig. 4). This discrepancy does not arise from the presence of undetermined higher $\beta 1 \rightarrow 4$ oligomers. This was demonstrated, as for purified cellulose, by eluting samples under conditions where the $\beta 1 \rightarrow 4$ oligomers readily elute [3]. Total sugars by the phenol–sulfuric acid method agreed closely with the total DNS sugars for the 45°C run. It has also been shown that the "front" peak contains no sugar measurable by the phenol–sulfuric acid method. The NP hydrolysates are apparently unique among the substrates tested thus far [4] in containing something which reacts with the DNS and phenol–sulfuric acid reagents, but which is bound to the μBONDAPAK columns, either not eluting at all or eluting over some hours or days.

DISCUSSION

High-performance liquid chromatography is a rapid, flexible and convenient method for analyzing cellulosic hydrolysates. Gas chromatography (GC) [9] would provide approximately the same speed and resolution in separating the three primary sugars, but would require considerably more sample preparation, including formation of volatile derivatives. Calculations from gas chromatograms are more difficult, because each sugar yields multiple peaks and the derivatization is seldom quantitative. It is also considerably more difficult to carry out preparative separations via GC. GC methods are considerably more sensitive and the multiple peaks are advantageous qualitatively. Thus, GC provides excellent backup for LC methods, especially in attempting to identify minor or trace sugars, after separation and collection via LC.

Kinetic data for sugar production from cellulosic wastes (such as in Fig. 4 for NP) will be required to design an economically feasible process for converting cellulosic wastes to usable end products. For example, since only about one-third of the Sweco-milled NP is susceptible to rapid hydrolysis in any case, it might be better to operate NP hydrolyses at 55–60°, to take advantage of the rapid hydrolysis of the susceptible portion at higher temperatures. Assuming that glucose is the desired product, the actual time-temperature regime selected would depend on the relative costs of the hydrolysis itself versus the costs for recovering the glucose from the mixture. Possibly a two-stage process is needed, rapidly producing a glucose-cellobiose mixture at 60°C in stage one, followed by the action of (immobilized?) β-glucosidase in stage two to convert the cellobiose to glucose. It would clearly be desirable to operate at 60°C (or perhaps even higher) if cellobiose was the desired product. Such considerations are, of course, tentative until additional data are obtained.

The lower glucose:cellobiose ratios at the higher temperatures presumably means that the $\beta 1 \rightarrow 4$ glucosidase which converts cellobiose to glucose is more susceptible to heat inactivation than the enzymes which catalyze the formation of cellobiose from cellulose.

REFERENCES

[1] M. Mandels, J. Kostick, and R. Parizek, in E. C. Jahn (Ed.), *Proceedings of the Seventh Cellulose Conference, (J. Polym. Sci. C, 36,* 445 (1971)), Interscience, New York, 1971.

[2] M. Mandels, L. Hontz, and J. Nystrom, *Biotechnol. Bioeng., 16,* 1471 (1974).

[3] J. K. Palmer, *Anal. Lett., 8,* 215 (1975).

[4] R. K. Andren, M. Mandels, and J. E. Mederios, "Production of Sugars from Waste Cellulose by Enzymatic Hydrolysis. Part I. Primary Evaluation of Substrates," this volume, p. 205.

[5] M. Mandels and E. T. Reese, *J. Bact., 79,* 816 (1960).

[6] L. Hough, J. K. N. Jones, and W. H. Wadman, *J. Chem. Soc.,* 1702 (1950).

[7] G. L. Miller, *Anal. Chem., 31,* 426 (1959).

[8] M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Anal. Chem. 28,* 350 (1956).

[9] J. R. Clamp, T. Bhatti, and R. E. Chambers, *Methods Biochem. Anal., 19,* 229 (1971).

LIGNIN IN MATERIALS

S. INGEMAR FALKEHAG

Westvaco Research Center,
North Charleston, South Carolina 29406

SYNOPSIS

Rising oil prices and the high energy intensity in production of synthetic polymers favors the future use of lignin or its derivatives in materials applications rather than for energy production. Although much basic and applied research is required to define better the materials related properties of lignin and its best uses in polymer systems, it is possible today to use modified lignins as phenol or polyol replacement in thermosetting resins and in the reinforcement of elastomers. The view is presented that the functional properties lignin exhibits in natural systems can well be used to meet human needs. The functions of lignin in wood as a reinforcing component and stabilizer against various stresses, including degradation, can be translated into products such as composite materials and antioxidants. Lignin is responsible for the storage of almost 40% of the solar energy bound in wood and is at a high enthalpic level as compared to many other wood or biomass components. The future use of a systems approach is advocated for the chemical treatment of plant materials to maximize for the value of all components, including lignin. A massive increase in research efforts is recommended for the wood and phytochemicals area, preferably through international activities, as the developments might benefit not only the industrialized nations, but also developing countries.

INTRODUCTION

Lignin is a major participant in energy flows in the biosphere. More solar energy is stored in lignin than in any other functional component in plants (if cellulose and hemicelluloses are classified as separate components). For a softwood with 42% cellulose, 27% hemicelluloses, 28% lignin, and 3% lipid extractives, the lignin will contribute to the enthalpy content (as heat of combustion) of the wood by about 39%, while the contributions by cellulose and hemicelluloses will be 34% and 22%, respectively. In spite of this, lignin (and phenolics in general) are often ignored in discussions of biomass and energy flows in biological systems [1]. Complementary to being a major component in plant systems for the storage of solar energy, lignin plays a major role as a composite material component in wood. It also has various functions in controlling stresses to which trees are subjected.

Man's uses of lignin in materials applications have been very limited, except together with the carbohydrates in lumber, board and unbleached paper. The

present U.S. consumption of forest products is about 300 million tons annually, which corresponds to 70 million tons of lignin. The kraft-pulping process is used for about 95% of the chemical pulp production in the U.S. Of the 16 million tons of lignin dissolved in the kraft-pulping operation, only a very small fraction is recovered, and the organic materials in the black liquor are burned in the recovery units in the mills with an obvious important contribution to the heat balance of the operation.

Large volume uses for kraft lignin other than for the generation of energy are most likely to be in materials applications. In order for such uses to occur, the value will have to be significantly higher than the heat value plus recovery and conversion costs for the lignin. Increasing oil prices will favor the uses of lignin in materials if the energy intensity in recovery and conversion is lower than for the corresponding petroleum- or coal-derived chemicals. This is likely to be the case, and lignin can be expected to be used in higher value applications than energy in the future. Properties related to the aromatic nature of lignin can be predicted to be an asset.

The approaches in using lignin in polymer and materials systems can vary. In principle, uses in both macromolecular form and as low molecular weight building stones after fragmentation are possible. As pointed out by Goldstein [2], those synthetic polymers which can be derived from lignin would require a lignin feed stock of about 16 million tons/yr, an interesting figure in light of the potentially equal available quantity of kraft lignin from U.S. kraft mills. However, a fragmentation approach in using lignin is likely to be more intensive in terms of both energy and capital than uses of lignin in macromolecular form, which should favor the latter approach whenever possible for technical reasons. Such questions are, however, matters of research which, in the case of lignin as a materials component, is only in its infancy. This paper deals primarily with potential uses of lignin in macromolecular form.

LIGNIN IN NATURAL SYSTEMS

The formation, distribution and chemistry of lignin in its native state is well reviewed elsewhere [3]. Wood constitutes an enormously intriguing and composite material, well designed to handle the stresses to which a tree is subjected. Little fundamental knowledge is available about the materials contribution of lignin in wood and the evolutionary development and role of lignin. The solar energy-driven synthesis of carbohydrates by carbon dioxide and water fixation is the starting point for the synthesis of aromatics and lignin over the shikimic acid pathway. The varying energy input for synthesis of plant components, starting with carbohydrates, and via various pathways leading to nucleic acids, proteins, aromatics, fatty acids and isoprenoids (in order of energy input and extent of reduction of the carbon compounds), must have a purpose in relation to the fitness of the plant. Only limited information is available on the thermodynamics of plant components, but certain principles can gradually be distinguished [1] as related to enthalpic and entropic levels of some biomass components. If heats of combustion are used as the measure of the enthalpic levels one can, from Table I, see that considerably more energy is put into the synthesis of lignin than that of cellulose, and that the lipids form the highest energy group. Cellulose, milled wood lignin, oleic acid and α-pinene can be seen as typical representatives of wood components.

TABLE I

Heats of Combustion for Various Compounds that can be Derived from Plants

Compound	Δ Hc (25°C)	
	BTU/Lb.	Cal/Gm
Methane	23,800	13,200
α-Pinene	19,600	10,900
Oleic Acid	17,000	9,500
Phenol	14,300	7,900
Ethanol	13,200	7,600
Lignin	12,700	7,100
Methanol	10,300	5,700
Cellulose	7,500	4,200
CO	4,400	2,400
CO_2	0	0

$$Compound + O_2 \xrightarrow{\Delta\ Hc} CO_2 + H_2O$$
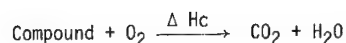
From a thermodynamic standpoint, order in biological systems does not have to mean crystallinity, but rather corresponds to complexity in macromolecular structure and function. It is likely that lignin not only is in a much higher enthalpy state than the carbohydrates, but that its entropy is lower. According to Morowitz [1], the more organized (ordered) a system is, the longer the energy is stored in the material on its way from the source to the (ecological) sink. A unique property of lignin is that it is very stable in nature and actually acts as a stabilizer towards various stresses to which the plant is subjected, e.g., as experienced by the inhibiting effect of lignin on the rate of enzymatic hydrolysis of wood.

Some of the functions or purposes of lignin in a plant system might be described in the following manner:

1. Energy (potential and entropic) storage system.
2. Response to mechanical stresses as a composite materials component.
3. Response to biochemical stresses by inhibiting enzymatic degradation of other components and low biodegradation susceptibility of the lignin itself.
4. Response to physical-chemical stresses by controlling water balances and plant response to humidity.
5. Response to chemical stresses by inhibiting atmospheric degradation and functioning as an antioxidant, an ultraviolet light stabilizer, and possibly also a flame retardant.
6. Contribution to soil properties during natural decay.
7. Purposeful interactions with other systems, including the meeting of human needs, the role in digestive systems in mammals, etc.

It is the contention of this article that the properties of lignin as demonstrated by its functions in plant and ecosystems can be increasingly used in situations related to human exosomatic activities, preferably without major changes in energy states.

ALTERNATIVE USES FOR LIGNIN

Higher wood prices and various other factors have in recent years raised the incentive of retaining more lignin and hemicelluloses in the fiber and the use of higher-yield fibers in papermaking. The trade-off point in increased yield can be said, in a simplified manner, to be when the cost of the incremental input of mechanical, chemical, and thermal energy (connected to process and capital costs) in the fiber producing process is equal to the incremental increase in value of the paper on some performance basis minus the loss in heat value of the pulping liquor. Thus, uses of lignin as an energy source and as a paper component are closely linked and the future trends towards higher yields are likely to be governed primarily by energy and capital costs.

With a broad conceptual view, lignin uses can be classified in the following manner:

1. Energy
2. Paper, board, etc.
3. Fragmentation and chemical conversion to:
     Vanillin and l-dopa, etc.
     Dimethylsulfide and dimethylsulfoxide
     Phenols and catechols
     Benzene derivatives
     Synthesis gas, etc.
4. Macromolecular uses in solution systems as:
     Dispersants
     Emulsion stabilizers
     Complexing agents
     Precipitants, coagulants, etc.
5. Macromolecular or particle uses in polymer materials systems such as:
     Thermosetting resins
     Rubber reinforcement
     Polyblends
     Stabilizer applications, e.g., as antioxidants
6. Matrix or gel applications involving:
     Adsorption
     Desorption, e.g., controlled release
     Ion exchange
7. Carbonization and pyrolysis to:
     Active carbon
     Carbon or graphite fibers and foams
8. Soil and fertilizer applications

The primary uses to date for isolated lignin products including lignosulfonates has been in area 4. Most other uses are highly dependent on the economic competitiveness with petroleum-derived products.

PROPERTIES OF KRAFT LIGNIN

Kraft lignin [3] is the term for a polydisperse [4], branched phenolic macromolecular composite derived from native lignin in the kraft-pulping process and iso-

TABLE II

Glass Transition Temperatures for Various Lignins as Measured by Torsional Braid Analyzer

Lignin	T_g °C
Unmodified Pine Kraft Lignin	180
Acetylated	133
Methylated With $(CH_3)_2SO_4$	128
Acetylated and Methylated (CH_2N_2)	118
Cross-linked and Acetylated	173

lated by precipitation with acid from the black liquor. It has a variety of functional groups [3], it is soluble in polar hydrogen-bond breaking solvents [4], it has high thermal stability and a high heat value; it is nontoxic; and it has a "hindered phenol" nature with some interesting redox properties. It is highly reactive in a variety of reactions involving the hydroxyls or the phenolic structure, etc., and can be modified to change solubility in various solvents, transition temperatures, mechanical properties, colloid and surface chemical characteristics, etc., according to application needs.

The glass transition temperature (T_g) for kraft lignin is greatly affected not only by changes in the molecular weight distribution, but also by blocking or elimination of various oxygen containing functional groups [5]. In Table II, the T_g (as measured by a torsional braid analyzer) is given for a pine-kraft lignin where the hydroxyl groups have been blocked by acetylation or methylation. Methylation of the carboxyl groups in an acetylated lignin gives a T_g as low as 118°C. The T_g of unmodified pine-kraft lignin in the acidic form is 180°C. It appears that internal hydrogen bonding is to a high degree controlling the thermal transitions of lignins.

The mechanical properties of lignins have not been studied as yet in any detail. As measured by the torsional braid analyzer [5], the elastic modulus for an unmodified pine kraft lignin has been determined to be about $2 \cdot 10^{10}$ dyn/cm^2 which is below the modulus for polystyrene and most thermoplastics. Failure properties
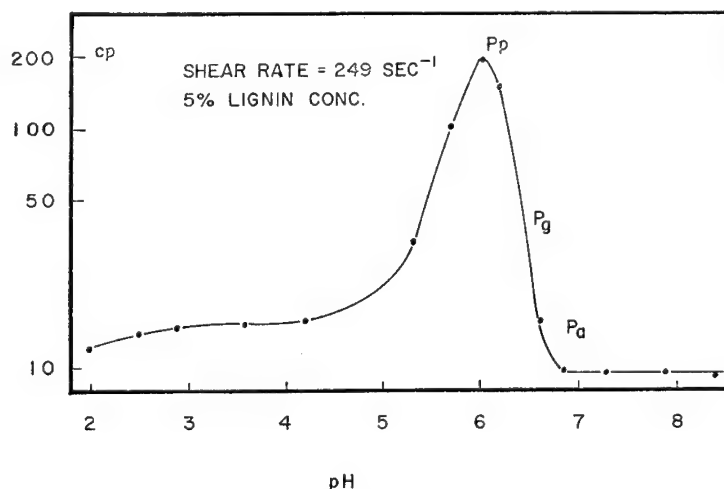
FIG. 1. Apparent viscosity during precipitation of lignin from an alkaline water solution.

are affected greatly by the dimensions and state of the specimen tested, but lignin can be considered to be a highly brittle polymer. This is not surprising, considering that the number-average molecular weight for the unmodified lignin is about 1600. In fine dimensions, such as the less than 1000 Å size particles in rubber reinforcement, the mechanical properties might be quite different from what is measured with conventional bulk specimens. Extensive research is still needed to characterize the physical properties of lignins in relation to various materials uses. The mechanical properties can be affected significantly by chemical modifications.

Precipitation of lignin from an alkaline water solution by acidification at low temperatures results in the formation of uniformly sized spherical particles with a diameter of 100–300 Å (depending on conditions). The highly hydrated particles coalesce at elevated temperatures into larger sized, irregularly shaped particles. As seen in Figure 1, the apparent viscosity of a 5% lignin solution during acidification starts to rise at slightly below pH 7 (point P_a), indicating association of the lignin macromolecules. At lower pH (P_g) gel formation is observed, and the Newtonian flow characteristics are lost. At pH 6 (P_p) precipitation of lignin particles can be observed [6].

The location of the precipitation point is affected by the electrolyte concentration in a linear manner, and a divalent ion such as calcium will be about 10 times more effective in changing the association and precipitation points to a higher pH than a monovalent ion such as sodium (analogous to the Schulze-Hardy rule for particles with ion effects on electrostatic potentials).

A hierarchy of events can be considered in the precipitation of lignin and in the following physical-chemical interactions of the particles, eventually followed by coalescence during heat treatment or drying. The hierarchy of entities to be considered in this process is defined below:

1. Lignin macromolecule
2. Associate (cluster or embryo) of macromolecules (P_a)
3. Gel formed by interactions of the associates (P_g)
4. Critical nucleus (smallest lignin particle)
5. Lignin particle formed by growth of the critical nucleus in the range of P_p.
6. Floc of lignin particles
7. Aggregate of flocs
8. Secondary particle systems formed after an eventual coalescence.

Figure 2 shows an electron micrograph of a precipitated lignin where the unit particles, the flocs and the aggregates can be recognized in some of the structures. The unit particle size is about 150 Å. It is amazing how some of the flocs with tentacles hanging together in aggregates resemble the flocs and aggregates recorded by Vold [7] and Sutherland [8,9] by computer simulation of random collisions of small spheres.

The ability to affect size and configuration of the lignin entities, from macromolecules to particle structures, might be of considerable importance in the uses of lignin in copolymer, polyblend, and particle reinforcement applications. Much more extensive research is required to gain a better insight into the underlying phenomena, their control, and their effect on final materials properties in composite structures. Some of the phenomena described are also likely to be of importance during the synthesis and deposition of lignin in situ in the tree and in affecting fiber and paper properties when lignin is retained in the carbohydrate system.
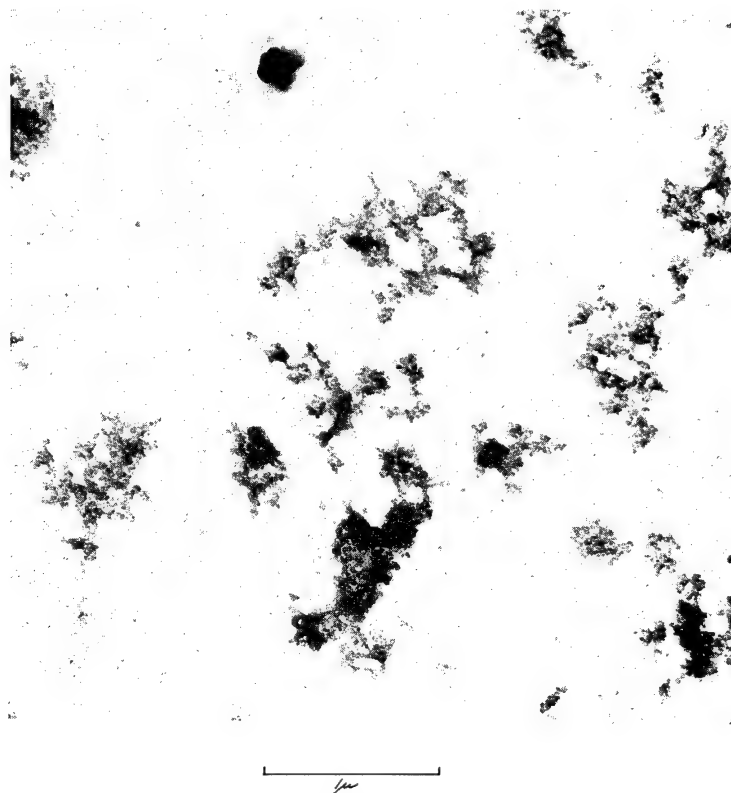
FIG. 2. Electron micrograph of a carefully dried lignin slurry at a magnification of 46,700.

KRAFT LIGNIN IN SYNTHETIC POLYMERS

From an entropic energy standpoint lignin should be used in macromolecular form whenever possible. Fragmentation of lignin by some energy source and rebuilding to a polymer structure will require energy but might have to be done in order to meet the requirements related to technical properties or process technology. Thermal fragmentation in the presence of a hydrogen donor will produce a more highly reduced product and raises the enthalpy level of the product as indicated in Table I, where simple phenol is located higher than lignin. Such a process will, of course, have a cost which, in the case of hydrogenation, can be considerable because of the high energy intensity in hydrogen production.

However, the uses of kraft lignin directly as a replacement for phenol in, e.g., thermosetting resins, introduces constraints in terms of acceptable level of replacement because of effects on resin viscosity, cure rate, etc. Mechanical properties will also be affected above a replacement level of 20% [5]. The properties of kraft lignin and resin formulation can, however, be modified to enable a higher degree of replacement. Some applications are not as sensitive to the constraints. Kraft lignin products are presently used in specific phenolic resin binder applications. The use of lignin as a phenol replacement might be particularly attractive in board applications. From an economic standpoint, the future is far from clear because of uncertainties regarding phenol prices, which will be highly dependent on oil
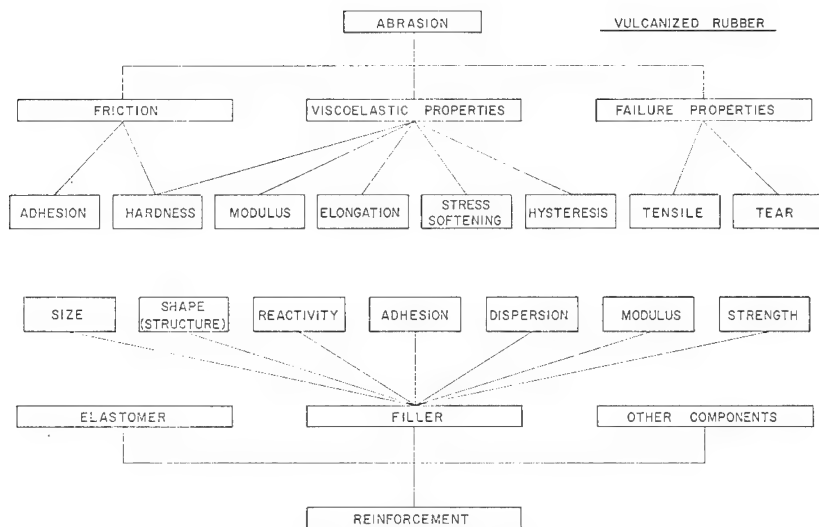
FIG. 3. Schematic analysis of the abrasion phenomena of rubber and the reinforcement process with emphasis on filler particle parameters.

prices and the potentially large volume production of phenol via the coal gasification process. The high energy intensity in phenol production via the cumene process makes it unlikely that phenol prices will drop below 25¢/lb.

Research on lignin-derived products in thermosetting resin applications involving phenolic resins or polyurethanes could dramatically affect the possible future uses of kraft lignin, and a major increase in efforts related to these materials applications is justified. A sound, scientifically based understanding of lignin as a macromolecule and its potential roles in materials systems is most desirable as a platform for applied studies.

Other properties besides chemical and physical properties are of importance in polymer applications. The dimensions of the lignin entity should be highly significant. In the thermosetting applications the lignin participates in a macromolecular state in a copolymer or graft manner. At high loadings the lignin might constitute a coherent "phase," but this would not be likely at loadings below 20%.

Most other potential applications of lignin in polymers involves the presence of lignin as a discontinuous phase as a particle or possibly associate of macromolecules. Polyblends might offer some interesting opportunities but will require sound R&D efforts. The primary particle application of interest would be as a reinforcing agent in elastomers replacing carbon black or other small particle size reinforcing fillers [6,10]. Looking at the hierarchy of lignin entities described in the discussion on lignin precipitation, uses for lignin can be visualized at any of these dimensions. Again, a more basic understanding on the theory of reinforcement and the relation of various particle or "entity" parameters to the composite material properties is desirable. Generally speaking, it is likely that lignin will have the greatest potentials in composites where it will constitute the higher modulus phase in a lower-modulus polymer. This might very well be one of the functions of lignin in wood, at least as related to its interaction with the hemicellulose

TABLE III
Physical Properties of Lignin and Carbon Black Reinforced Styrene–Butadiene Rubber at
68 Parts Lignin per 100 Parts Rubber (Oil-Extended SBR)

	Lignin A	Lignin B	HAF	ISAF
Modulus (psi)	520	650	610	730
Tensile Strength (psi)	3165	3380	2500	2930
Elongation (%)	720	630	720	750
Tear Resistance (ppi)	355	300	320	335
Hardness (Shore A)	54	54	56	61
Corrected Pico Abrasion	86	85	91	114

system. In such a case, we would have an example of the "imitation of nature" when we use lignin as a reinforcing agent.

Some of the particle (filler) parameters involved in the reinforcement of rubber are schematically outlined in Figure 3, where an attempt also has been made to analyze the abrasion process in terms of some of the underlying physical properties that could affect performance [6]. Abrasion resistance is of primary concern in the final use of vulcanized rubber in tire applications. Lignin can give a high tensile strength as compared to carbon black, as can be seen from Table III. In fact, it turns out that in the case of lignin-reinforced styrene–butadiene rubber (SBR) the abrasion resistance is governed, not by the failure properties, but by the viscoelastic properties. Particle size will affect the former more than the latter, and no correlation could be established between the observed particle size in the rubber and the abrasion resistance. Particle shape (structure) and mechanical properties of the filler might rather be the limiting parameters.

One of the more convenient and effective processes for incorporation of lignin into a rubber is by precipitation cocoagulation with a rubber latex. A uniform distribution of very small particles (down to 100 Å diameter) can be obtained as seen in Figure 4, an electron micrograph produced from a carefully prepared sample where lignin coalescence during drying was prevented by a thin film-drying technique. Figure 5 demonstrates the sizes and dispersion of lignin particles in a vulcanized final rubber sample. The average particle size is still below 1000 Å.

From a technical standpoint, lignin can well compete with carbon blacks in rubber reinforcement. Until now the economics and the competitiveness with the petroleum based carbon black has not been adequately attractive. It is possible that lignin should be used in specific elastomers or applications where properties unique for lignin can be exploited.

Modified lignins can be used effectively as atmospheric stabilizers (antioxidants) in elastomers [11]. This is another demonstration of a human use of a particular property of lignin that most likely is operating in the natural system. Lignin has a unique hindered phenol structure which can exert antioxidant effects and shows synergism with peroxide decomposers such as alkyl phosphites.

It is quite possible that in the attempted uses of lignin to meet polymer or materials needs one should not just try to "replace" a synthetic component, but to take new innovative approaches where the uniquenesses of lignin as a macromolecule should be exploited. This will require a much better understanding of the structure-property-requirement relationships for various lignin containing composites.

FIG. 4. Electron micrograph of a carefully dried lignin-SBR latex precipitation cocoagulation product at a magnification of 46,700.

Regarding the future competitiveness of lignin and other natural polymers with oil- or coal-derived polymers, the new economic balances might affect choices of raw materials and types of products to be used. It is also possible that natural products can have an advantage with regard to minimum plant size, capital investment and process costs, energy intensity in production, etc. The present polymer industry is highly energy intensive. One should also question the need to manipulate with carbon-oxygen-hydrogen balances in natural products (see Table I) and determine whether materials needs actually have to be met with polymers with the high enthalpic energy levels many of our synthetic products have today. In a society concerned with the correct use of energy (ortho concept), we should try to stay low on the enthalpy scale in meeting needs and not increase entropy by unnecessary breaking of covalent bonds in naturally occurring polymers. Natural systems can teach us something about materials and optimum design. Obviously lignin and other plant polymers also have a great long-term asset by being solar energy-derived, renewable, and ecologically desirable.

The incentives in developed countries for using renewable resources rather than oil as raw materials appears to be rising. However, the incentives might be still greater in developing countries (not controlling oil) where biomass production rate is high, and an integrated systems approach could be taken in the use of renewable resources for both food, chemicals, fuel and materials. One can foresee the day
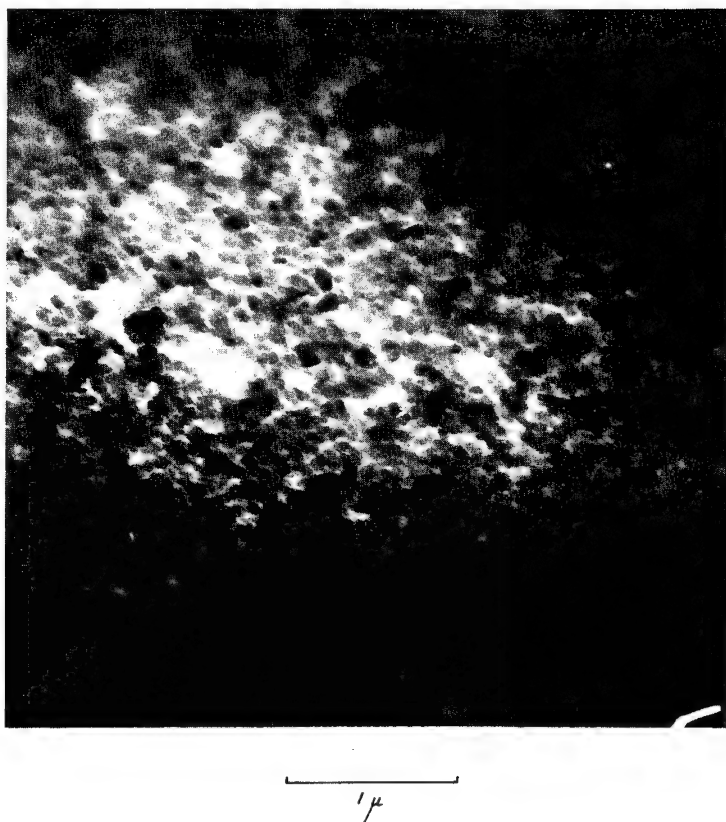
FIG. 5. Electron micrograph of a vulcanized lignin-SBR sample at a magnification of 45,700.

when chemical treatment of wood and biomass will be done, not only to produce paper and energy, but to create sets of products with an optimum combined value to society. The lignin from the enzymatic hydrolysis of biomass might have a considerable value. We should not forget that lignin constitutes almost 40% of the solar energy stored in plants.

REFERENCES

[1] H. J. Morowitz, *Energy Flow in Biology,* Academic Press, New York, 1968.
[2] I. S. Goldstein, ACS Symposium on *Renewable Resources for Plastics* April 7-9, 1975, pp. 25–43.
[3] K. V. Sarkanen and C. H. Ludwig, *Lignins,* Wiley-Interscience, New York, 1971.
[4] W. Brown, *J. Appl. Polym. Sci., 11,* 2381, 1967.
[5] A. de Ruvo and S. I. Falkehag, unpublished results.
[6] S. I. Falkehag, ACS meeting, Los Angeles, March 28, 1971.
[7] M. J. Vold, *J. Colloid Sci., 18,* 684 (1963).
[8] D. N. Sutherland, *J. Colloid Interphase Sci., 22,* 300 (1966).
[9] D. N. Sutherland, *J. Colloid Interphase Sci., 25,* 373 (1967).
[10] S. I. Falkehag and D. V. Braddon, ACS Symposium on Renewable Resources for Plastics, April 7-9, 1975, p. 68–72.
[11] D. V. Braddon and S. I. Falkehag, in B. Sedláček (Ed.), *Mechanism of Inhibition Processes in Polymers: Oxidative and Photochemical Degradation,* Interscience, New York, 1973, p. 101.

PERSPECTIVES ON PRODUCTION OF PHENOLS AND PHENOLIC ACIDS FROM LIGNIN AND BARK

IRVING S. GOLDSTEIN

Department of Wood and Paper Science,
North Carolina State University,
Raleigh, North Carolina 27607

SYNOPSIS

The formation of phenols from lignin has been studied for almost sixty years. Various lignins (hydrolysis, alkali, sulfite, kraft) from both softwoods and hardwoods have been subjected to pyrolysis, alkali fusion, hydrogenation, and hydrolysis. Although yields of phenols as high as 50% of the lignin have been reported, commercial production has not taken place, largely because the products are complex mixtures with many components. In this paper, two avenues which could lead to commercial practice are pointed out: (1) applications research to use more of the lignin conversion products in the way coal tar has been utilized in the past, and (2) reforming the complex mixtures by catalytic processing to yield simpler, more marketable compounds in the manner of the petroleum industry. Phenolic acids are obtainable in high yield from pine bark. Utilization of this material could result from its conversion into smaller, more reactive fragments followed by resin and adhesives applications research.

INTRODUCTION

The recognition that lignin can be degraded into phenolic materials has stimulated almost sixty years of research on the conversion of lignin into phenols. This work has had two objectives; the elucidation of the composition and structure of lignin, and the production of useful materials from waste lignin. Generally, investigators have been concerned with one of these objectives or the other. Although the structure workers have succeeded, so we now know the origin of the phenolic lignin fragments encountered, the commercial practice of converting lignin to phenols has not been attained.

Despite hundreds of papers from all over the world, with the USSR contributing about half those published since 1960 as they attack the lignin residues from wood hydrolysis plants, a viable commercial process has not emerged. In large measure this has been the result of the complex product mix from lignin degradations as well as falling synthetic phenol prices (just under \$0.20/lb in the 1950s to \$0.08/lb in 1972) as giant cumene process plants have come on stream. Now that syn-

259

thetic phenol has climbed back to $0.27–$0.33/lb in response to high petroleum prices and shortages, a reappraisal of lignin-to-phenol processes is in order. The present paper is not concerned with the technical merits of specific processes, but seeks to point out approaches for broadening the product base from any process and increasing its value.

LIGNIN CONVERSION PROCESSES

A compilation of lignin conversion processes is given in Table I. While not exhaustive, the table is representative of the processes described in the literature. Lignin types include hydrolysis (HCl and H_2SO_4), alkali, sulfite, and kraft from both hardwoods and softwoods. The lignins have been subjected to destructive distillation at atmospheric or reduced pressure and in air or in reducing or inert atmospheres. They have been pyrolyzed and fused with salts or alkali. Hydrogenation has been carried out using diverse catalysts, temperatures, solvents and acidity or alkalinity. Hydrolysis has been effected under acid, alkaline or neutral conditions. Enzymatic degradation of lignin has not been included in the table since preparative enzyme reactions have not been reported.

LIGNIN CONVERSION PRODUCTS

Table I also contains information about the yields and qualitative composition of the crude products obtained from the lignin conversion processes. The phenolic fractions are further described in Table II which again is representative rather than exhaustive.

The yields of soluble products from lignin range from 10–100% of the lignin with the higher yields generally being associated with the more expensive hydrogenation processes. Only a portion of the soluble tars are phenolic in nature with maximum values reported in the range of 50% of the weight of the lignin. However, closer examination indicates that much of these high phenolic yields consist of nonvolatile phenols. Actual yields of distillable phenols are closer to 35% [14,46] and may consist of as many as 10–15 of the compounds listed in Table II.

Consequently, the yield of any single component is inclined to be rather small and insufficient to provide enough revenue to support the entire process. For example, Goheen [37] in his improvements on the Noguchi process obtained 3% phenol, 4% o-cresol and 6% m,p-cresol in a total monophenol yield of 21%. This 13% yield of readily marketable phenols would have had to be improved by about 50% to have been profitable at the time of the study.

Similarly, of the 7.1% identifiable phenols resulting from neutral hydrolysis of kraft lignin [51] a catechol yield of 3.6% was obtainable, including that derivable from guaiacol by acid cleavage of the methyl ether. Despite the much higher value of catechol market uncertainties prevented commercialization.

In both examples cited above the economic analyses were based entirely on the value of the low yields of the phenols named. Neglected were the other phenolic components, light oils, acids, neutral oils, heavy oils, and pitches which make up the bulk of the products from these and other lignin conversion processes listed in Table I.

TABLE I
Production of Phenols from Lignin

Reference	Lignin	Process	Soluble Tar (%)	Phenols (%)	Neutral Oils (%)
1) Heuser & Skioldebrand (1919)	Hydrolysis	Destructive Distillation	15.7		
2) Fischer & Schrader (1920)		Dry Distillation	12	4.1	1.6
3) Fischer & Schrader (1921)		Sodium Formate Fusion	22.3		
4) Tropsch (1921)	Hydrolysis	Vacuum Distillation	10.2	3.8	
5) Heuser & Herrmann (1924)		Alkali Fusion under H in Fe		21.3	
6) Fierz-David & Hannig (1925)		Distillation with H & Catalysts	17.8	6.9	3.8
7) Bowen & Nash (1926)		Hydrogenation	37	4.8	
8) Phillips (1929)	Alkali	Destructive Distillation	18	15	1.3
9) Phillips (1931)	Alkali	Distillation with Zn in H	16	9	
10) Phillips & Goss (1932)	Alkali	Vacuum Distillation under CO_2	28.3	9.8	4.1
11) Moldavskii & Vainshtein (1935)		Hydrogenation	44		
12) Bridger (1938)	Alkali	Destructive Distillation	19.5	9.6-17	1.5-8
13) Hachihama et al. (1940)	Hydrolysis	Hydrogenation	46.7		
14) Freudenberg & Adam	Spruce hydrolysis	Distillation with H & Catalysts	62	35	7
15) Freudenberg, Lautsch et al. (1941)	Spruce hydrolysis	Hydrogenation	55	15	40
16) Hachihama & Jodai (1941)	Spruce hydrolysis	Hydrogenation	70	26	17.5
	Beech hydrolysis		50	13.5	3
17) Hachihama & Jodai (1941)	Softwood	Hydrogenation	75-80	33	
18) Takahashi & Matsuda (1945)	Larch hydrolysis	Hydrogenation	68.5	49.1	
19) Harris, Saeman et al. (1949)	Hardwood soda	Hydrogenation	75	8-10	65
20) Shorygina et al. (1949)		Metallic Na in NH_3	39	21.6	8
21) Swiss Patent 305,712 (1955)	Sulfite	Hydrogenation	28	14	
22) Giesen (1956)	Scholler Sulfite	Hydrogenation	41-3 / 45	16.5 / 22.5	
23) Giesen (1957)	Scholler	Hydrogenation		47.5	
24) Panasyuk (1957)	Hydrolysis	Thermolysis	38	10-12	
25) Zarubin & Tishchenko (1960)	Hydrolysis	Alkaline hydrolysis	108	20	
26) Oshima et al. (1961)	Sulfite	Hydrogenation	77	11-28	5-28
27) Sakakibara & Araki (1961)	Hydrolysis Alkali	Hydrogenation		47.3 / 61.7	
28) Enkvist et al. (1962)	Kraft	Alkaline hydrolysis	50	38	
29) Panasyuk et al. (1962)	Hydrolysis	Alkaline distillation		11.6-20.3	8.2-15.5
30) Ploetz et al. (1963)		Hydrogenation		21	36
31) Sakakibara (1963)	Hydrolysis	Hydrogenation		45	
32) Rieche et al. (1964)	Alkali & hydrolysis	Hydrogenation	75	14	
33) Sukhanovskii et al. (1964)	Hydrolysis	Thermal decompn.	17.7	7	
34) Akhmina et al. (1965)	Hydrolysis	Thermal decompn.	10-19	5-9.5	2-4
35) Oshima et al. (1965)		Hydrogenation	85		
36) Sukhanovskii et al. (1965)	Spruce hydrolysis	Thermolysis	18	8-9	2-4.5
37) Goheen (1966)	Sulfite	Hydrogenation	65	21	9

Table I. (*continued*)

Reference	Lignin	Process	Soluble Tar (%)	Phenols (%)	Neutral Oils (%)
38) Oshima et al. (1966)	Sulfite	Hydrogenation		29.2	
39) Reznikov & Morozov (1966)		Pyrolysis	22	11.5	7
40) Bronovitskii & Kalinskaya (1967)	Pine	Hydrogenation	73.5	47	26
41) Bronovitskii et al. (1968)	Spruce Willstaetter	Hydrogenation	60-70	42-49	
42) Clark & Green (1968)	Kraft	Alkaline hydrolysis	70	11	
43) Bhaskaran & Schuerch (1969)	Whole maplewood	Alkaline hydrogenation	72	35	
44) Hellwig et al. (1969)	Kraft	Hydrogenation		46	14
45) Lapai et al. (1969)	Hydrolysis	Hydrogenation		50	42
46) Schweers (1969)	Spruce hydrolysis	Hydrogenation		52	32
	Beech hydrolysis			36	40
47) Kirshbaum & Domburg (1970)	Aspen	Pyrolysis		12	
48) Lundquist (1970)		Acid hydrolysis		17	
49) Murashkevich et al. (1970)	Hydrolysis	Pyrolysis		15-17	
50) Benigni & Goldstein (1971)	Kraft softwood	Hydrogenation	38-58	3.6-13.3	3.0-22.0
51) Benigni & Goldstein (1971)	Kraft softwood	Neutral hydrolysis	11-54	7.1	
52) Bronovitskii et al. (1971)	Spruce hydrolysis	Hydrogenation	85.7	40	22
53) Domburg et al. (1971)	Alkali aspen	Vacuum pyrolysis	51.1	6.8	
54) Nimz et al. (1971)	Beechwood	Acid & Alkaline hydrolysis & hydrogenation	91	37	
55) Bronovitskii & Kalinskaya (1972)	Spruce Willstaetter	Hydrogenation	80	35	35
56) San John & Dobrev (1973)	Hydrolysis	Hydrogenation		46.2	

COAL TAR UTILIZATION

The composition of lignin conversion products is somewhat reminiscent of the tar recovered from the coking of bituminous coal [57]. Phenol, cresols and xylenols comprise 2.2% of the tar, light oils (benzene, toluene, xylenes, etc.) 2.0%, neutral oils 36%, tar bases 2.3%, and pitch and resins 57%. Over 300 compounds have been identified from the carbonization of coal, most of which occur in the coal tar.

The utilization of coal tar depended for its economic success not only on the extraction of low yields of pure chemicals which formed the basis of the coal-tar chemical industry, but also on useful applications for the bulk of the material. In 1940, chemicals accounted for only 4.8% of the total tar distilled. Creosote and other distillates, road tars, pitch, crude and refined tars and pitch coke accounted for 95.2% of the total tar. Unless uses had been found for these materials, the coal tar industry would not have developed.

By analogy, utilization of the lignin conversion products other than simple phenols would provide a broader product base to support the raw material and processing costs. Under such circumstances phenols from lignin could become a commercial reality. Tars from the conversion of lignin appear to be less complex than coal tars and contain a higher proportion of phenolic materials.

TABLE II
Mononuclear Phenols Obtained from Lignin[a]

	Yield, % of Lignin
Phenol	1.8 (40), 5.5 (14), 3 (37)
o-Cresol	4 (37), 5.9 (40), 5 (52)
m-Cresol⎫ p-Cresol⎭	6 (37), 16.5 (40), 14 (52), 25 (56)
o-Ethylphenol	1 (37), 4.7 (40)
m-Ethylphenol	(38)
p-Ethylphenol	1.1 (14), 3.5 (37), 7 (40)
p-Propylphenol	2 (37), 2.4 (40)
2,4-Xylenol	0.6 (19), 1.25 (37)
2,5-Xylenol	(38)
2,6-Xylenol	(38)
3,4-Xylenol	(38), (41)
3,5-Xylenol	(12), (38)
3-Methyl-4-Ethylphenol	0.75 (40)
Catechol	21.3 (5), 2.9 (14), 31.6 (31), 5.5 (42), 3.8 (50)
Hydroquinone	(41)
4-Methylcatechol	1.1 (14), 2 (42)
4-Ethylcatechol	0.3 (19), 1 (42)
4-Propylcatechol	0. 25 (19)
Guaiacol	3.9 (14), 3.5 (42), 4.4 (46)
4-Methylguaiacol	7.1 (14), 6.5 (46)
4-Ethylguaiacol	1.6 (14), 11.2 (46)
4-Propylguaiacol	0.9 (19), 9.9 (46), 7 (54)
Isoeugenol	1.3 (14)
Syringol	3.5 (46), 2.3 (47)
4-Methylsyringol	1.8 (46), 3.0 (47)
4-Ethylsyringol	6.7 (46), 1.0 (47)
4-Propylsyringol	6.8 (46), 24 (54)

[a]References in parentheses.

APPLICATIONS RESEARCH ON LIGNIN CONVERSION PRODUCTS

The applications research on the neglected portions of the lignin degradation products can take the form of utilization of additional pure components or of mixtures. Among the pure components isolatable, 4-methylcatechol has been re-

ported in 1–2% yield. It has been found to be an excellent monomer for phenolic resins [58].

The total hydrogenolysis product can be condensed with formaldehyde to form impregnating resins [41]. Fractions have shown antioxidant properties for polyethylene [52] and gasoline [59]. Lignin tar pitches have been used in battery cases and for electrode carbon [60], and lignin oils have been applied as wood preservatives [61] and fungicides [62]. Other fractions have shown herbicidal [63] and insecticidal [64] activity.

As much as 25% of the lignin subjected to neutral hydrolysis [51] ends up as oligomers (averaging three aromatic rings) with catechol functionality. Such material would seem to be an ideal candidate for an antioxidant in roofing pitches, road asphalts and tars and dark pigmented polyolefins. At $0.10/lb it would return as much value to the process as the 3.6% yield of catechol at $0.70/lb.

The possibilities for utilizing the lignin conversion products other than simple phenols have been only cursorily examined and merit further effort.

REFORMING OF LIGNIN CONVERSION PRODUCTS

Instead of finding uses for the lignin conversion products other than simple phenols, an alternative route to greater value would be secondary processing of these materials to form marketable compounds in the manner that petroleum fractions are reformed.

Hellwig et al. [44] have projected a yield of about 35% pure phenol based on lignin if the mixture of phenols and catechols obtained in 46% yield from continuous hydrogenation of lignin were used as feedstock for hydrodealkylation and hydrodehydroxylation processes. Based on commercial experience with hydrodealkylation and published literature on the hydrodealkylation and hydrodehydroxylation of phenols to phenol, they believe that conversion of the mixture of phenols from lignin can be accomplished with high selectivity. It may be argued that hydrodealkylation alone with retention of catechol functionality in a portion of the product would result in a greater overall value.

The hydrocracking of the lignin tar from the Noguchi process has been shown to increase the yield of valuable phenols [65], and the hydrocracking of lignin pyrolysis tar has provided a reaction product consisting entirely of aromatic and naphthenic hydrocarbons with no unsaturation, no oxygen compounds, and no sulfur compounds [66]. Among the 31 aromatic hydrocarbons identified was benzene.

In view of the great body of knowledge available in catalytic reaction technology, future progress in lignin tar conversion to useful compounds should be very rapid.

PHENOLIC ACIDS

Phenolic acids are high molecular weight phenols which contribute to the Klason "lignin" content of bark, but differ from lignin in their lower molecular weight, alkali solubility caused by high carboxyl content, and lower methoxyl content [67,68]. They are easily extracted from bark by alkali and may comprise almost 50% of the weight of the bark of conifers.

Attempts to utilize these readily available materials have for the most part involved the crude extracts. Applications have included dispersing agents [69], viscosity control [70], drilling mud components [71], and resins and adhesives [72,73]. Considerable effort has been expended on technically useful resins and adhesives from phenolic acids compatible with phenolformaldehyde resins, but the extent of their use is not know. Hemingway [74] has studied the phenolic acids of southern pine bark and concluded that their molecular size is too large for satisfactory resin formation. Depolymerization to smaller more reactive fragments seems to be needed.

Alkaline fusion of phenolic acids has yielded phloroglucinol and catechol [68], while guaiacyl, catechol and p-hydroxyphenyl derivatives have resulted from hydrogenolysis [75]. Degradation of phenolic acids to simpler structures which would be more useful might be accomplished by any number of the processes listed in Table I. Applications research would be necessary to optimize resin and adhesives properties.

CONCLUSION

Commercial production of phenols from lignin has been prevented by the complexity of the products obtained and the low cost of synthetic phenol. With higher synthetic phenol prices now in effect, production of phenols from lignin could become a reality if the product base is broadened by utilization of the other materials besides the simple phenols obtained from lignin, or by further conversion of these fractions into useful compounds. Wide utilization of phenolic acids from bark will probably depend on their degradation to simpler structures.

REFERENCES

[1] E. Heuser and C. Skioldebrand, *Z. Angew. Chem., 32*(1), 41 (1919).

[2] F. Fischer and H. Schrader, *Gesammelte Abh. Kenntnis Kohle, 5,* 106 (1920).

[3] F. Fischer and H. Schrader, *Brennst. Chem., 2,* 161 (1921).

[4] H. Tropsch, *Gesammelte Abh. Kenntnis Kohle, 6,* 293 (1921).

[5] E. Heuser and F. Herrmann, *Cellul. Chem., 5,* 1 (1924).

[6] H. E. Fierz-David and M. Hannig, *Helv. Chim. Acta, 8,* 900 (1925).

[7] A. R. Bowen and A. W. Nash, *Fuel Sci. Pract., 5,* 138 (1926).

[8] M. Phillips, *J. Amer. Chem. Soc., 51,* 2420 (1929).

[9] M. Phillips, *J. Amer. Chem. Soc., 53,* 768 (1931).

[10] M. Phillips and M. J. Goss, *Ind. Eng. Chem., 24,* 1436 (1932).

[11] B. L. Moldavskii and S. M. Vainshtein, *Khim. Tverd. Topl., 6,* 656 (1935).

[12] G. L. Bridger, *Ind. Eng. Chem., 30,* 1174 (1938).

[13] Y. Hachihama, S. Jodai, and M. Umezu, *Kogyo Kagako Zasshi, 43,* 127 (1940).

[14] K. Freudenberg and K. Adam, *Ber., 74B,* 387 (1941).

[15] K. Freudenberg, W. Lautsch, G. Piazolo, and A. Scheffer, *Ber., 74B,* 171 (1941).

[16] Y. Hachihama and S. Jodai, *Kogyo Kagaku Zasshi, 44,* 773 (1941).

[17] Y. Hachihama and S. Jodai, *Kogyo Kagaku Zasshi, 45,* 302 (1942).

[18] T. Takahashi and T. Matsuda, *J. Soc. Text. Cellul. Ind. Jap., 1,* 646 (1945).

[19] E. E. Harris, J. F. Saeman, and C. B. Bergstrom, *Ind. Eng. Chem., 41,* 2063 (1949).

[20] N. N. Shorygina, T. Y. Kefeli, and A. F. Semechkina, *Dokl. Akad. Nauk. SSSR, 64,* 689 (1949).

[21] Swiss Patent 305, 712, March 16, 1955.

[22] J. Giesen, U.S. Patent 2, 774, 795, Dec. 18, 1956.

[23] J. Giesen, Swiss Patent 318, 446, Feb. 28, 1957.

[24] V. G. Panasyuk, *Zh. Prikl. Khim., 30,* 598 (1957).

[25] M. Zarubin and D. Tishchenko, *Zh. Prikl. Khim., 32,* 395 (1959).

[26] M. Oshima, Y. Maeda, and K. Kashima, German Patent 1, 115, 737, Oct. 26, 1961.

[27] A. Sakakibara and T. Araki, *Mokuzai Gokkaishi, 7,* 19 (1961).

[28] T. Enkvist, J. Turunen, and T. Ashhorn, *Tappi, 45,* 128 (1962).

[29] L. V. Panasyuk, V. G. Panasyuk, M. Ya. Zarubin, and D. V. Tishchenko, *Izv. Vyssh. Ucheb. Zaved. Les. Zh., 5*(2), 132 (1962).

[30] T. Ploetz, H. Richtzenhain, W. Deiters, and J. Giesen, German Patent 1, 142, 853, Jan. 31, 1963.

[31] A. Sakakibara, Japanese Patent 26, 668, Dec. 28, 1963.

[32] A. Rieche, L. Redinger, and K. Lindenhayn, *Monatschr. Deut. Akad. Wiss. Berlin, 6*(6), 430 (1964).

[33] S. I. Sukhanovskii, E. I. Akhmina, E. B. Evstifeeva, T. A. Podgornaya, A. I. Kalnins, K. Abele, I. Alsups, A. I. Kul'kevits, and O. Kiselis, *Khim. Pererab. Zashch. Drev., 1964,* 87.

[34] E. I. Akhmina, E. S. Benzmozgin, A. G. Nemchenko, T. A. Podgornaya, S. I. Sukhanovskii and Y. D. Yudkevich, *Khim. Tekhnol. Topl. Prod. Ego Pererab., 1965,* 12.

[35] M. Oshima, Y. Maeda, and K. Kashima, U.S. Patent 3, 223, 698, Dec. 14, 1965.

[36] S. I. Sukhanovskii, E. I. Akhmina, T. A. Podgornaya, and Z. I. Lisina, *Sb. Tr. Vses. Nauch. I-ssled. Inst. Gidroliz. Sul'fitno Spirt. Prom., 13,* 274 (1965).

[37] D. W. Goheen, "Hydrogenation of Lignin by the Noguchi Process," in *Lignin Structure and Reactions,* Advan. Chem. Ser., *59,* 205 (1966).

[38] M. Oshima, K. Kashima, T. Kubo, H. Tabata, and H. Watanabe, *Bull. Chem. Soc. Jap., 39*(12), 2750, 2755 (1966).

[39] V. M. Reznikov and E. E. Morozov, *Khim. Pererab. Drev., 22,* 10 (1966).

[40] V. E. Bronovitskii, and L. Kalinskaya, *Uzb. Khim. Zh., 11*(2), 31 (1967).

[41] V. E. Bronovitskii, M. A. Volschkovich, L. L. Kalinskaya, and A. Nam, *Uzb. Khim. Zh., 12*(3), 71 (1968).

[42] I. T. Clark and J. Green, *Tappi, 51*(1), 44 (1968).

[43] T. A. Bhaskaran and C. Schuerch, *Tappi, 52*(10), 1948 (1969).

[44] K. C. Hellwig, S. B. Alpert, C. A. Johnson, and S. C. Schuman, *Production of Phenols from Lignin,* Technical Association of the Pulp and Paper Industry, Annual Meeting, New York, New York, February 18, 1969.

[45] A. P. Lapai, V. F. Safonov, and N. I. Nazarova, *Izv. Nauch. Issled. Inst. Nefte-Uglekhim., 1969 (11),* Pt. 1, 81.

[46] W. Schweers, *Holzforschung, 23*(1), 5 (1969).

[47] I. Z. Kirshbaums and G. Domburg, *Latv. PSR Zinat. Akad. Vestis, 1970 (2),* 43.

[48] K. Lundquist, *Acta Chem. Scand., 24*(3), 889 (1970).

[49] T. V. Murashkevich, A. I. Skrigan, and A. I. Khat'ko, *Vests. Akad. Nauk. Belaruss. SSR, 1970 (1),* 80.

[50] J. D. Benigni and I. S. Goldstein, *J. Polym. Sci. C 36,* 477 (1971).

[51] J. D. Benigni and I. S. Goldstein, *J. Polym. Sci. C 36,* 467 (1971).

[52] V. E. Bronovitskii, L. L. Kalinskaya, and D. R. Ikramova, *Gidroliz Lesokhim. Prom., 24*(8), 14 (1971).

[53] G. Domburg, I. Kirshbaums, and V. N. Sergeeva, *Khim. Drev., 7,* 51 (1971).

[54] H. Nimz, K. Das, and N. Minemura, *Chem. Ber., 104*(6), 1871 (1971).

[55] V. E. Bronovitskii and L. L. Kalinskaya, *Khim. Prir. Soedin., 8*(1), 106 (1972).

[56] L. San John and S. T. Dobrev, *Tsellyul. Khartiya, 4*(4), 22 (1973).

[57] E. O. Rhodes, "The Chemical Nature of Coal Tar," in H. H. Lowry (Ed), *Chemistry of Coal Utilization,* Vol 11, pp. 1287–1370, John Wiley, New York, 1945.

[58] G. E. Troughton, J. F. Manville, and S. Z. Chow, *For. Prod. J., 22*(9), 108 (1972).

[59] B. M. Gikht, I. V. Larconov, and V. K. Shitkov, *Neftepererab. Neftekhim., 1965 (4),* 11.

[60] V. G. Kashirskii, N. B. Lobacheva, and A. S. Malomuzh, *Nauch. Tr. Saratov. Politekh. Inst., 50,* 73 (1971).

[61] L. P. Azhar and E. D. Levin, *Derevoobrab. Prom., 20*(3), 17 (1971).

[62] L. P. Azhar, E. D. Levin, and N. A. Sokolova, *Izv. Vuz. Lesnoi Zh., 15*(3), 118 (1972).

[63] L. P. Azhar and E. D. Levin, *Izv. Vuz. Lesnoi Zh., 14*(3), 91 (1971).

[64] M. I. Goryaev, L. I. Tret'yakov, M. G. Pugachev, A. P. Popov, and G. P. Kornilova, *Tr. Inst. Khim. Nauk. Akad. Nauk. Kaz. SSR, 27,* 3 (1970).

[65] K. Hastbacka and J. B. Bredenberg, *Pap. Puu, 55*(3), 129, 133 (1973).

[66] A. V. Rachinskii and E. D. Levin, *Izv. Vuz. Lesnoi Zh., 17*(1), 111 (1974).

[67] E. F. Kurth and J. F. Smith, *Pulp Pap. Mag. Can., 55*(12), 125 (1954).

[68] M. D. Fahey and E. F. Kurth, *Tappi, 40*(7), 506 (1957).

[69] K. R. Gray and H. L. Crosby, U.S. Patent 2, 782, 241, Feb. 19, 1957.

[70] E. Farber, U.S. Patent 2, 744, 024, May 1, 1956.

[71] C. C. Heritage and L. E. Dowd, Canadian Patent 581, 604, Aug. 18, 1959.

[72] F. W. Herrick and L. H. Bock, U.S. Patent 3, 025, 250, Mar. 13, 1962.

[73] A. B. Anderson, A. Wong, and K. T. Wu, *For. Prod. J., 24*(7), 40; *24*(8), 48 (1974).

[74] R. W. Hemingway, private communication.

[75] M. Sogo, *Mokuzai Gakkaishi, 12*(2), 96 (1966).

LIGNIN AS A RAW MATERIAL FOR SYNTHETIC POLYMERS

J. JOHAN LINDBERG, VÄINÖ A. ERÄ, and TUURE P. JAUHIAINEN

Department of Wood and Polymer Chemistry,
University of Helsinki, SF-00100,
Helsinki 10, Finland

SYNOPSIS

A brief review is given on various methods to produce technically useful polymers and plastics from lignin and their low molecular degradation products. The synthesis, chemical and physical properties of thermostable and thermoplastic polymers from low molecular weight lignophenols are discussed on the basis of several examples, including polyimides, polyphenylene oxides and aromatic polyesters. It is concluded that the physical properties of the polymers are not considerably influenced by the methoxy group characteristic for the lignophenols.

INTRODUCTION

Because of the unfavorable rheological and chemical properties of the lignins obtained from wood by various methods of isolation, they have not generally been used as such for the manufacture of technically useful polymers and plastics. They have instead found comparatively large uses as cheap fillers and additives. In the cellulose manufacturing process the residual lignin is used as a fuel and energy source for the process. The basic price of this raw material has therefore also increased together with the worldwide increase of cost of fuels. Therefore, to be able to use lignin and its degradation products for other purposes than a fuel, e.g., as raw materials for polymers and plastics, the resulting products must have a higher degree of refinement, quite contrary to the state of affairs only a few years ago.

In the past, a number suggestions and patents have appeared concerning the use of lignins and their low molecular degradation products as a source for the manufacture of technically useful polymers and plastics. This is especially the case with lignosulfonic acids, but many processes of the kind mentioned have also been proposed for kraft lignin. Among the various ways to use lignins as raw materials or polymers are as component in phenol-formaldehyde resins [1]; as the basic ma-

269

terial in lignin-styrene graft polymers [2]; as the chief component in the manufacture of fibers and graphite fibers from lignosulphonic acid and methyl metacrylate [3]; and in the manufacture of thermostable and thermoplastic polymers [4].

The above examples indicate that lignins may be used to synthesize both thermosetting resins and thermoplastics which have properties of very similar nature as those obtained from petrochemicals. The raw material may be either the high molecular weight lignin or its low molecular, phenolic degradation products.

THERMOSTABLE THERMOPLASTICS

Much evidence seems to indicate that in most cases, the synthesis of thermostable thermoplastics is most easily achieved by using the low molecular phenolic degradation products of lignin rather than its high molecular weight fractions. The following discussion will therefore be chiefly concerned with such polymer syntheses, especially with those developed at the Department of Wood and Polymer Chemistry and the Department of Chemistry of the University of Helsinki during the years 1967–1974.

By comparing the thermal properties of various low molecular aromatic compounds, it was concluded long ago that linear poly-m- and -p-phenylene compounds (Structure I) should have especially favorable thermal properties.

m-

I

p-
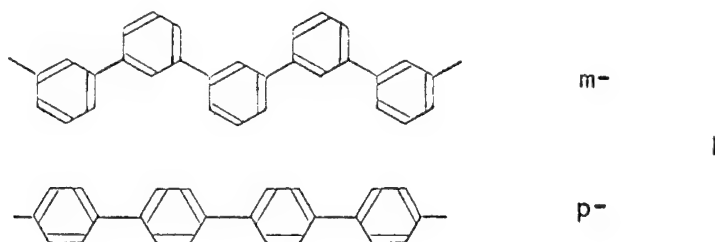
Later synthetic work indicated that the softening point of the polymers is in the temperature region of 770°K (500°C). It was further shown that their processing properties are rather poor due to their brittleness and stiffness.

On the other hand, polymers with better processing properties were obtained by introducing other chemical groups between the aromatic unit of the chain (Structure II). In this way the thermal properties were only slightly impaired and the

I I
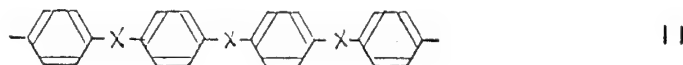
processing properties were markedly improved owing to the increased flexibility of the polymer chain [5].

THERMOSTABLE POLYMERS

Polyimides

As an example of the polymers illustrated above, aromatic polyimides may be mentioned. Penttinen [6] studied the synthesis, thermal and mechanical proper-
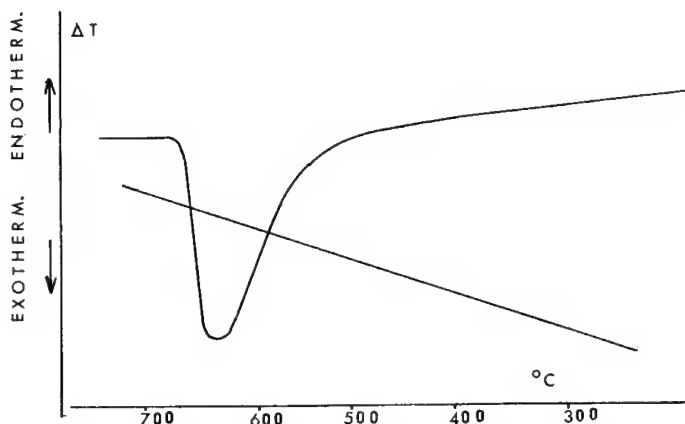
FIG. 1. Differential thermal analysis of a polypyromellitimide prepared from p-aminophenyl p-amino-benzoate, sample weight 5.5 mg and heating rate 7.7°C/min.

ties of aromatic polyimides (Structure IV) from nitrophenols which may be obtained by nitration of lignin or sawdust [7,8]. He proposed the following reaction sequence.
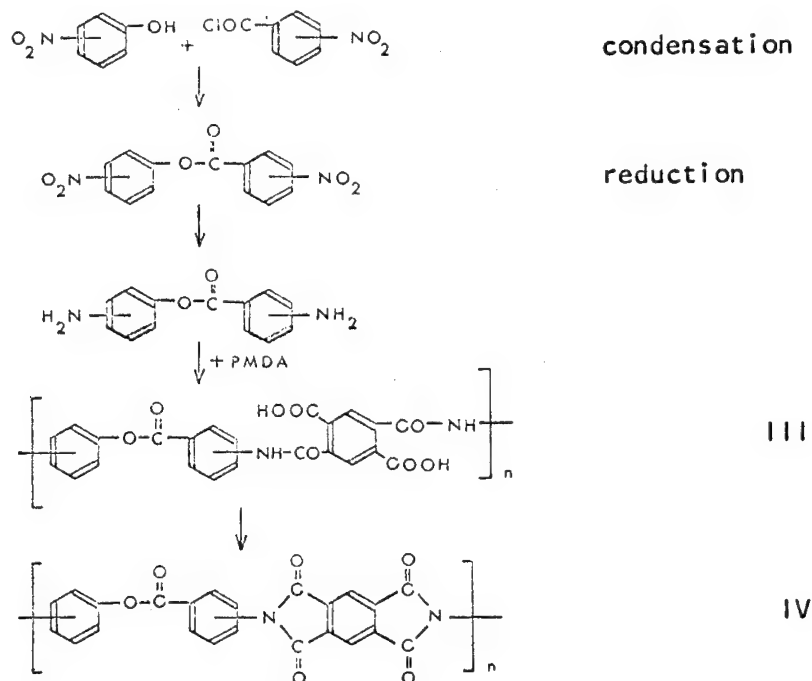
Nine new polypyromelliteamideacids (Structure III) and their polyimide derivatives (Structure IV) were synthesized from various o-, m-, and p-substituted aminophenylbenzoates. It was found that the polymers were thermally stable up to 720°K (450°C) (Fig. 1 and Table I). The polymers could be processed to weakly yellowish, transparent and lucid films which showed good mechanical strength properties.

TABLE I

Data from Differential Thermal Analyses of the Polypyromellitimides Prepared from Diamines

Compound	T^1 °C	T^2 °C	$\triangle H$ kcal/g	S	n
p-Aminophenyl p-aminobenzoate	465	631	5.6	0.22	0.59
m-Aminiphenyl p-aminobenzoate	415	550, 594	4.4	-	-
o-Aminophenyl p-aminobenzoate	390	516, 576	6.4	0.22	0.59
p-Aminophenyl m-aminobenzoate	450	562, 632	5.7	0.17	0.52
m-Aminophenyl m-aminobenzoate	425	616	5.2	0.39	0.79
o-Aminophenyl m-aminobenzoate	380	504, 566	7.1	0.55	0.93
p-Aminophenyl o-aminobenzoate	415	547, 622	6.0	0.70	1.05
m-Aminophenyl o-aminobenzoate	415	564	6.0	0.29	0.68
o-Aminophenyl o-aminobenzoate	290	538, 601	5.5	0.49	0.88

T^1 = temperature where decomposition began; T^2 = peak temperatures; $-\Delta H$ = heat of thermal degradation; S = shape index; and n = order of main reaction according to Kissinger.

Polyphenylene Oxides

2,6-disubstituted phenols are found in considerable amounts, 0.2–1.0%, in spent black liquors [9,10]. These types of phenolic compounds may easily be converted to high molecular weight polymers in high yield with oxygen in the presence of amine complexes of copper salts as catalyst.

2,6-Disubstituted polyphenylene oxides (Structure V) and various quinones are formed, of which 3,3′, 5,5′-disubstituted diphenoquinone (Structure VI) is the chief product.

The amount of undesired diphenoquinone and other quinones obtained in the reaction is determined by the magnitude and polarity of the substituents R. The reaction temperature, the solvent, the complexing amine and the ligand–metal ratio of the catalyst, are summarized in Table II and in the literature [4,11].

Polyphenylene oxides are generally synthesized from 2,6-dimethyl- and 2,6-diphenylphenols, but as found recently using Ag_2O-triethylamine catalyst, the 2,6-methoxyphenol gives comparable yields of polymers with good physical properties [12]. Thus it is found by thermodynamic studies [13] that there is a greater flexi-

TABLE II

Influence of Substituents on the Products and Reaction Path When Using O_2 and Copper-Amine Catalysts

| | Substituent | | σ_p [b] | Chief product [a] | | $\bar{M}_n$ | $[\eta]$ |
	2-	6-		Yield %			dl/g
1.	$-OCH_3$	$-OCH_3$ [c]	-0,54	Q 74, P 2		5 900	
2.	$-CH_3$	$-OCH_3$	-0,44	P 60		13 100	0,27
3.	$-tC_4H_9$	$-tC_4H_9$	-0,40	Q 97			
4.	$-CH_3$	$-tC_4H_9$	-0,37	Q			
5.	$-CH_3$	$-CH_3$	-0,34	P 89		31 000	0,72
6.	$-CH_3$	$-C_2H_5$	-0,32	P		25 400	0,40
7.	$-CH_3$	$-iC_3H_7$	-0,32	P		15 350	0,24
8.	$-C_2H_5$	$-C_2H_5$	-0,30	P		32 000	0,53
9.	$-CH_3$	$-C_6H_5$	-0,18	P			
10.	$-C_6H_5$	$-C_6H_5$	-0,02	Q (traces)			0,05
11.	$-CH_3$	$-Br$	+0,06	P			0,03
12.	$-CH_3$	$-Cl$	+0,06	P		71 000	0,47
13.	$-CHO$	$-OCH_3$	(+0,23)	no reaction			
14.	$-Cl$	$-Cl$	+0,46	no reaction			
15.	$-COCH_3$	$-OCH_3$	+1,04	no reaction			
16.	$-NO_2$	$-NO_2$	+1,56	no reaction			
17.	Copolymerization:		1+5, 2:1	Q 77, P 7			

[a] P = Polymer, Q = Diphenoquinone.

[b] Hammett's σ_p — constant. It is assumed that the p-parameters can be used also for ortho-positions.

[c] When using Ag_2O in triethylamine as catalyst, $\bar{M}_n$ = 70,000–180,000, yield 75%.

Reaction temperature, 273–293°K; solvent, pyridine or pyridine-nitrobenzene.

bility of the polymer chain in poly(2,6-dimethoxyphenylene oxide) than in poly(2,6-dimethylphenylene oxide) and also a greater free volume. However, the thermal and fiber-forming properties of the former polymer seem to be nearly equal to the latter one under similar conditions.

Aromatic Polyesters

The synthesis of aromatic polyesters from vanillin derivatives was attempted long ago. Recently it was found that by coupling, high temperature-resistant aromatic polyesters are formed which melt in the region 500–550°K [14]. Polyesters from vanillin may be prepared by two procedures:

Procedure I. Stage 1. Oxidation of vanillin to vanillic acid. Stage 2. Esterification of the dibasic acid. Stage 3. Condensation-polymerisation of the dibasic acid.

Procedure II. Stage 1. Same for Stage 1, Procedure I. Stage 2. Transformation of vanillic acid into its hydroxyethyl ether. Stage 3. Condensation polymerisation of the above compound.

The reactions leading to the formation of polyesters using the Procedures I and II can be presented as follows:

Procedure I

Procedure II
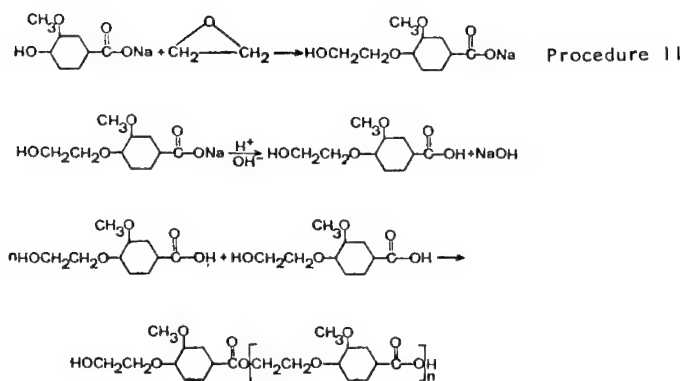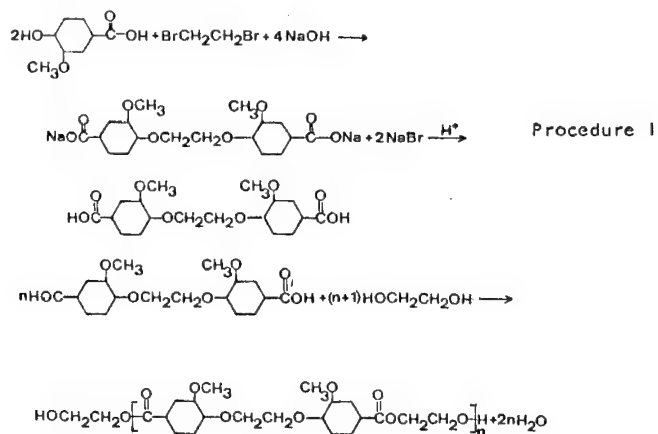
TABLE III

Viscosimetric Molecular Weights ($\overline{M}_v$) of Polyesters Prepared from Vanillin

Polyester	Condensation Temperature, °C	Polymerisation Time hrs	$[\eta]$ [b] g/dl	$\overline{M}_v$
Polyester I	220	22	0.0995	10 700
Polyester I [a]	180	5		
	220	20		
	250	20	0.125	26 300
Polyester II	280	22	0.166	37 200

[a] Polymerized by stepwise heating at the abovementioned temperatures.
[b] In m-cresol at 50°C.

TABLE IV
Melting Points and Glass Transition Points of the Polyesters

Polyester	Condensation Temperature,°C	Polymerisation Time, hrs	Tm, °C [b]	Tg, °C [b]	Tm°K/ Tg°K
Polyester	220	22	182	45	1.43
Polyester I [a]	180	5			
	220	20			
	250	20	201	74	1.36
Polyester II	280	22	227	66	1.47

[a] Polymerized by stepwise heating at the abovementioned temperatures.
[b] Scan speed 16°C/min.

Depending on condensation temperature and polymerisation time polymers were formed which showed thermoplastic properties comparable with poly(ethylene terephtalate) (Tables III and IV).

CONCLUSIONS

The polymers discussed above indicate clearly that phenols of lignin origin may be used equally well as phenols from petrochemical origin for synthesis and manufacture of thermostable and termoplastic polymers. Introduction of a methoxy substituent in the polymer chain seems not to conspicously impair physical and technical properties of the compounds.

REFERENCES

[1] T. U. Enkvist, Finnish Pat. 37402 (June 30, 1969).
[2] T. Koshijima, and E. Muraki, *J. Jap. Wood Res., 12* (3), 193 (1966); *13* (8), 355 (1967).
[3] M. Mansmann, German Pat. 2118488 (April 16, 1971).
[4] J. J. Lindberg and A. Savolainen, *Kem. Teollisuus, 26* (1), 25 (1969).
[5] A. H. Frazer, *High Temperature Resistant Polymers,* New York, 1968.
[6] K. Penttinen, *Reactivities of Nitrophenyl Nitrobenzoates and Aminophenyl Aminobenzoates in Relation to Polypyromellitimide Formation,* Dissertation, Univ. of Helsinki, 1970.
[7] C. Gustafsson and L. Andersen, Pap. Puu, *37* (1), 1 (1955).
[8] L. Andersen, *Soc. Sci. Fenn., Commentat. Phys.-Math, 19, 1* (1956).
[9] D. W. Goheen and J. B. Martin, U.S. Pat. 3375 283.
[10] W. R. Forsman, *Finska Kemistsamfvndets Medd., 81,* 47 (1972).
[11] J. J. Lindberg and T. P. Jauhiainen, *TTA Tutkimus ja Tekniikka-Forskning och Teknik, 32,* (1975).
[12] J. J. Lindberg, T. P. Jauhiainen, and A. Savolainen, *Pap. Puu, 54* (3), 911 (1972).
[13] A. Savolainen, *Thermodynamic and Relaxation Studies on 2,6-Disubstituted Polyphenylene Oxides,* Dissertation, Univ. of Helsinki, 1974.
[14] V. A. Erä and J. Hannula, *Pap. Puu, 56* (5), 489 (1974).

UTILIZATION OF PHENOL LIGNIN

WILHELM VORHER and WERNER H. M. SCHWEERS

*Universität Hamburg and Institut für Holzchemie
und chemische Technologie des Holzes,
205 Hamburg 80, Leuschnerstr. 91 b,
Federal Republic of Germany*

SYNOPSIS

Phenol lignin—the organic matter formed during phenol pulping of wood—was obtained from the spent liquor as a solid residue after distillation of the unreacted phenol. As a sulfur-free product of high molecular weight, phenol lignin was considered to be a suitable starting material for pyrolytic processes to obtain mixtures of phenol and lower methyl and methoxyl substituted phenols.

Pyrolysis of different fractions of phenol lignin and sodium lignophenolate was studied in a batchwise and in a continuous process. Mixtures of simple composition phenols were obtained in yields of approximately 30%. Yield and composition of the mixtures make it possible to apply a phenol pulping process which is self supporting in pulping chemicals; an eventual surplus of mixtures of simple phenols could find other uses.

INTRODUCTION

It has been known since 1919 that lignified material can be pulped by treating it with phenol, or mixtures of phenols, in the presence of catalytic amounts of acids [1,2]. Until recently, no attempt had been made to apply phenol-pulping on a technical scale. Searching for sulfur-free pulping processes, phenol-pulping was investigated by one of the authors and the influence of the cooking conditions on yield and quality of pulp was studied [3,4].

In this process phenol lignin is formed by acidolysis of the wood lignin and condensation of phenol in the ortho- or para-positions to its phenolic OH-group with the α-hydroxyl groups of the propane side chains of the lignin [5]. In this way a sulfur-free lignin is obtained. Phenol lignin may contain up to 25%–30% of condensed phenol [6,7,8], which makes the economy of any phenol-pulping process uncertain for the present; due to a considerable loss of pulping chemicals. Our investigations on the possibility of the utilization of phenol lignin were, therefore, directed to the production of phenolic compounds. Pyrolysis seems to be a suitable method to reach this goal. On the one hand, pulping chemicals spent during phe-

277

TABLE I
Analytical Data of Phenol Lignins

Lignin	Analytical data (%)	
Crude phenol lignin (cPL)	Phenol lignin A (PL-A)	Phenol lignin B (PL-B)
Pine-oxalic acid: 100 %	60	40
total OH	11,5	–
phenolic OH	5,5	12,0
$-OCH_3$	10,1	–
$\bar{M}_n$	2.500	–
Pine-HCl 100 %	40	60
total OH	13,0	12,7
phenolic OH	5,8	10,0
$-OCH_3$	10,0	3,6
$\bar{M}_n$	1.870	255
Beech-oxalic acid		
total OH	11,6	–
phenolic OH	4,5	–
$-OCH_3$	13,5	–
$\bar{M}_n$	1.795	–
Beech-HCl		
total OH	11,4	–
phenolic OH	5,9	–
$-OCH_3$	14,1	–
$\bar{M}_n$	2.080	

nolysis are recovered, while on the other hand, the relatively low-condensed phenol lignin (Table I) is cracked to a mixture of useful monomeric phenols.

If the utilization of phenol lignin in this way should yield sufficient phenolic products to render the pulping process self-supporting in pulping chemicals, excess phenol lignin could be used as a starting material for production of resins.

EXPERIMENTAL

Preparation and Characterisation of Phenol Lignins

Crude phenol lignin (CPL) was obtained as a residue from the waste liquors of pulping pine wood (*Pinus sylvestris*) and beech wood (*Fagus silvatica*) with phenol after recovery of the unspent amount of phenol by distillation.

In all experimental cooks, wood chips of industrial size were pulped, using a wood-to-liquor ratio of 1 to 4, 0,05% HCl or 2% oxalic acid as catalysts, and employing a cooking time of 3 hr at 160° to 170°C. Analytical data for different

phenol lignins are known from the literature [6,7], but such characterizations have been accomplished on specially prepared samples, which are not representative for byproducts obtained under the present pulping conditions. The crude phenol lignin was dissolved in acetone (10 ml acetone for 1 g of lignin) and precipitated by drops in the fourfold volume of permanently stirred ether. In this way ether-insoluble phenol lignin A (PL-A) and ether-soluble phenol lignin B (PL-B) were separated. The ether solution was decanted from the precipitated PL-A, which was stirred twice more with fresh ether. The remaining matter was filtered and washed with ether until the filtrate remained colorless. The residue of PL-A was dried in a Scheibler's desiccator. PL-B was recovered from the combined ether solutions by evaporating them to dryness. Table I shows the composition of CPL in terms of these two fractions. Phenol lignins A and B of different crude products were analyzed for total [9] and phenolic hydroxyl contents [10], methoxyl groups [11] and molecular weight [12]. The results obtained are also presented in Table I.

It is evident from the methoxyl contents and molecular weights that PL-A and PL-B obtained under pulping conditions are not equally suitable for pyrolysis. Obviously, PL-B represents a fairly degraded phenolysis product. According to its methoxyl content it consists of phenyl propane units which are condensed with up to four molecules of phenol [6]. PL-A represents the essential lignin matter of crude phenol lignin. When different catalysts were used for pulping the same wood species, the PL-A's obtained did not show much variation of their analytical composition, but different analytical data were obtained if different wood species were pulped.

We found later, in the course of our investigations on the suitability of phenol lignin for pyrolysis in a continuously working kiln, that the low softening point of the crude product (100°C) as well as that one of PL-A (150°C) caused a rapid plugging of the kiln in spite of the variation of all changeable process conditions. Sodium lignophenolates were therefore prepared by stoichiometric conversion of CPL, PL-A and PL-B from pine with 1N NaOH at room temperature. Crumbling brown powders were recovered from the aqueous solutions by evaporating (40°C, 12 mm Hg) and drying the solids obtained. Sodium lignophenolate (SLP) sinters at 300°C and is therefore a suitable material for continuous pyrolysis.

Microscale Pyrolysis of Phenol Lignin

Preliminary tests were carried out on a microscale to study the behavior of CPL, PL-A and PL-B under pyrolysis conditions. It was expected that PL-B was the main source for a recovery of phenol by pyrolysis of the crude product, while PL-A as the essential lignin matter should yield a mixture of monomeric phenols under thermal cracking. The amount of phenols obtainable by the degradation of PL-A accordingly should be higher than the quantity condensed with this lignin-fraction during phenol pulping.

Initial investigations were carried out with CPL, PL-A and PL-B of pine wood, subjecting them to pyrolysis at different temperatures in the glass apparatus illustrated in Figure 1. In each experiment up to 250 mg of lignin were pyrolyzed for 10 min in the focus of an electric heater. The temperature was controlled by a thermocouple on the outer wall of a 10 ml flask. A slow flow of nitrogen (60 bub-

VORHER AND SCHWEERS

F

N₂

T

E

C: Dry ice cooled condenser
E: Electric heater
F: 10-ml-flask
T: Thermo couple

C   C
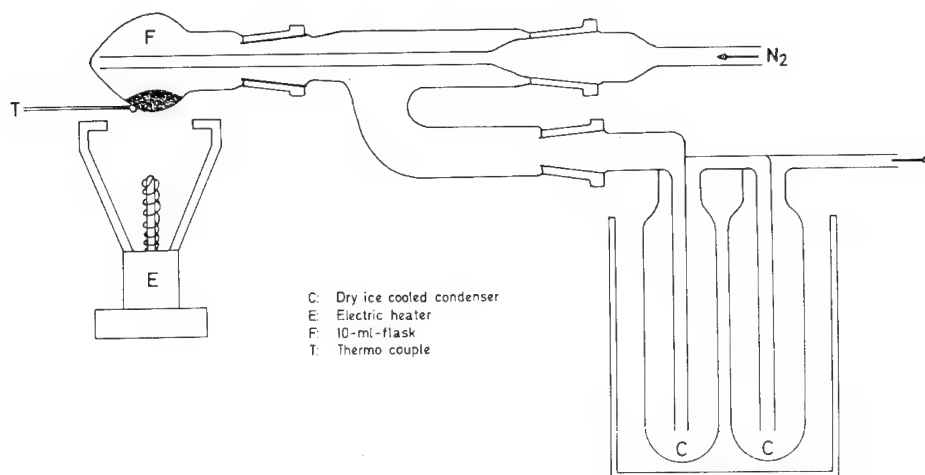
FIG. 1. Glass apparatus for microscale pyrolysis of phenol lignin.

bles per min) removed the pyrolyzate from the pyrolysis zone as quickly as it was formed to avoid its further decomposition. The pyrolyzate was conducted to two condensers cooled with dry ice. An oily condensate was obtained, which contained ether-soluble and ether-insoluble compounds. Noncondensable gases left the condensers. The pyrolysis residue was recovered from the reaction flask. The ether-soluble pyrolyzate was analyzed by high pressure liquid chromatography on silica-gel-60 to establish its relative content of monomeric phenols. The results obtained are presented in Table II.

Before subjecting sodium lignophenolate to continuous pyrolysis, the behavior of crude sodium lignophenolate (CSLP) was also studied by a microscale pyrolysis. The phenolic compounds were obtained from the pyrolyzates after extraction

TABLE II

Pyrolysis Products Obtained by Microscale Pyrolysis of Phenol Lignin

Temperature (°C)	Product pyrolyzed	1 Solid resid. (%)	2 Uncond. gas (%)	3 Ether-insol. pyrolyzate (%)	4 Ether-soluble pyrolyzate (%)	5 Monomeric phenols (%)
370	CPL	28	10	6	56	28
	PL-A	47	11	3	39	13
	PL-B	13	18	3	76	33
420	CPL	23	5	2	70	26
	PL-A	35	7	5	53	14
	PL-B	10	6	4	80	32
470	CPL	22	23	3	52	21
	PL-A	35	24	2	39	13
	PL-B	10	18	1	71	28
520	CPL	22	20	2	56	24
	PL-A	33	29	2	36	12
	PL-B	10	19	2	69	26

a Percent of starting lignin.
b Percent of ether-soluble pyrolyzate.

TABLE III
Phenolic Products Obtained by Microscale Pyrolysis of Crude Sodium Lignophenolate

Tempe- rature, °C	Pyrolysis residue, %	Phenols, % of Na-free lignin	Total phenols, %				
			Phenol	o-Cresol	p-Cresol	Guaja- col	Ethyl- -phenol
400	52	16,4	59	13	10	12	6
430	56	17,3	53	14	12	12	9
460	56	27,9	62	15	6	10	7
500	50	30,4	69	9	6	9	7

of the organic acids and neutral products. The yields are calculated on the basis of weight of sodium-free lignin and are presented in Table III.

The phenolic fractions were analyzed by GLC [13]. Evidently, pyrolysis of SLP yields phenol, o-cresol, p-cresol, guajacol, and ethyl phenol in reproducible amounts only.

Description of a Continuously Working Pyrolysis Apparatus

For large scale investigations on the thermal degradation of phenol lignin, a continuously working pyrolysis apparatus, illustrated in Figure 2, was used. The kiln was designed according to recommendations of Goheen and Martin [14].

The purpose of the equipment employed was to assure a rapid pyrolysis of the material fed to the kiln, and to insure a continuous and rapid removal of the pyrolyzate formed from the pyrolysis zone in order to avoid its further decomposition to a useless mixture of organic material. As seen in Figure 2, any type of phenol lignin is fed by a proportioning funnel (4) into a conduit, which opens into the pyrolysis kiln. A screw conveyor (5) driven by a motor (6) at a suitable speed (up to 120 rpm) carries the material through the pyrolysis zone, which corresponds to the length (60 cm) of the surrounding electric resistance heater (3). This jacket con-

1 Gas admission

2 Electric resistance heater (~900°C)

3 Electric resistance heater — separate heating zones surrounding pyrolysis kiln (~900°C)

4 Substance inlet (proportioning funnel)

5 Screw conveyor

6 Electric motor with infinitely variable speed transmission

7 Solid residue receiver

8 Condenser

9 Receiver

10 Outlet for noncondensable gas
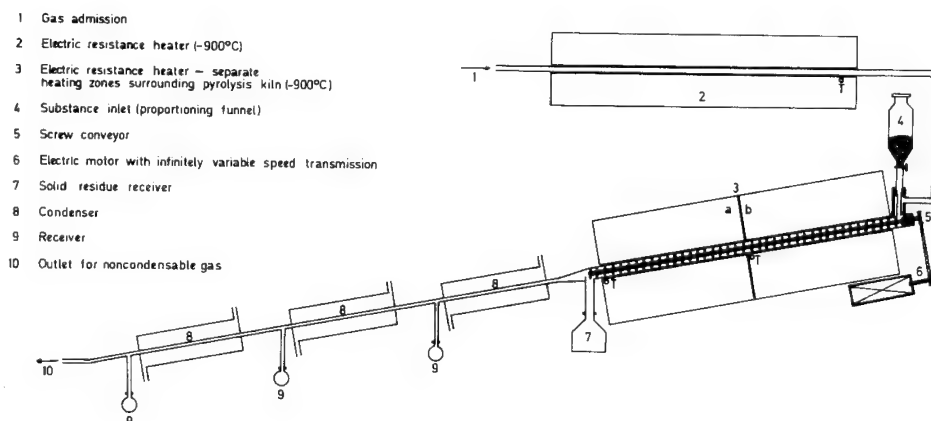
FIG. 2. Sectional side view of a continuously working pyrolysis plant.

TABLE IV

Products Obtained by Continuous Pyrolysis of SLP (in % of Sodium-free Lignin)

Temper., °C	Product pyro- lyzed	Pyrolysis residue, %	Ether- insol. pyroly- zate, %	Ethersoluble pyrolyzate, %			
				Total	Org.acids	Neutrals	Phenols
450	SLP-A	51,3	1,2	21,7	3,0	7,0	11,7
500	SLP-A	54,3	1,1	18,5	2,4	7,3	8,8
550	SLP-A	49,3	1,5	19,8	3,0	5,7	11,1
600	SLP-A	40,6	1,0	21,3	2,5	5,4	13,4
650	SLP-A	44,0	0,8	17,5	1,5	3,6	12,4
700	SLP-A	43,2	0,8	14,2	0,8	2,4	11,0
550	cSLP	39,3	0,2	28,7	1,6	6,7	20,4
650	cSLP	41,1	0,1	22,6	1,4	4,8	16,4

sists of two heating zones (3a and 3b) which can be heated either together or separately. By heating both zones equally, a symmetric temperature profile is produced in the kiln. Thus, a maximum temperature is obtained in the center, while only 40% of this value is reached at both ends of the kiln. The solid residue emitting from the pyrolysis zone is received into a flask (7). Inert gas is introduced into an admission conduit (1) and prehated by an electric resistance heater (2). Afterwards it sweeps through the kiln, carrying with it the pyrolyzate formed in the pyrolysis zone. It is conveyed into a battery of condensers (8), by which a fractional condensation of the pyrolyzate into special receivers is effected (9).

I Temp. of pyrolysis: 450°C   II Temp. of pyrolysis: 700°C
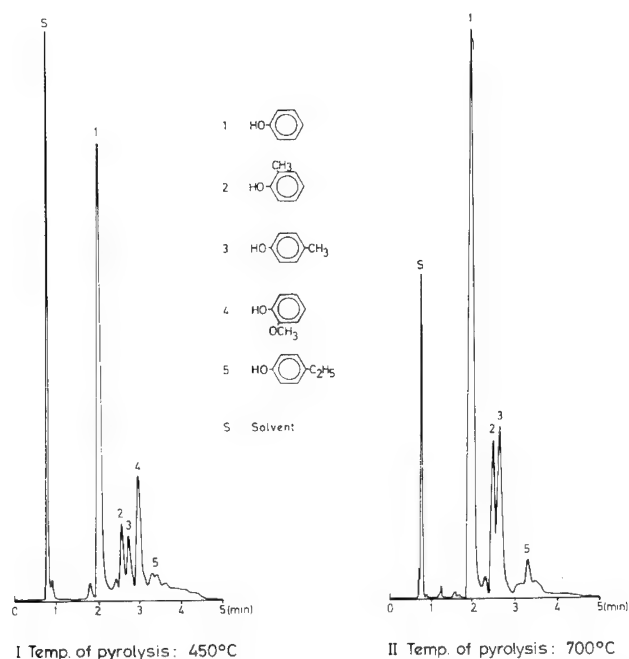
FIG. 3. Gas chromatograms of phenolic fractions obtained by pyrolysis of SLP-A.

TABLE V
Quantitative Composition of the Phenolic Pyrolyzate Fractions

Temp., °C	Product pyro- lyzed	Phenols, % (Total yield)	Phenols, % of total yield				
			Phenol	o-Cresol	p-Cresol	Guajacol	Other
450	SLP-A	11,7	60,0	9,0	5,5	25,5	-
500	SLP-A	8,8	56,4	10,9	12,7	13,6	6,4
550	SLP-A	11,1	66,1	17,9	12,5	-	3,5
600	SLP-A	13,4	64,6	16,9	13,9	-	4,6
650	SLP-A	12,4	62,5	14,1	17,2	-	6,2
700	SLP-A	11,0	62,5	14,4	18,8	-	4,3
550	cSLP	20,4	63,1	19,2	13,8	-	3,9
650	cSLP	16,4	64,3	14,3	14,3	-	7,1

Noncondensable gases are removed via a conduit (10). The kiln is inclined 15° to aid in moving the material through the pyrolysis zone. Measurement and control of temperature is affected by thermocouples placed on the points marked (T) in Figure 2. It is possible to carry out pyrolysis at temperatures up to 900°C.

Continuous Pyrolysis of Sodium Lignophenolate

Thirty grams of crude sodium lignophenolate (CSLP) and sodium lignopheno-late-A (SLP-A) were subjected to a continuous pyrolysis at temperatures between 450° and 700°C in the kiln illustrated in Figure 2. During all pyrolytical experiments a gas flow rate of 250 ml N_2/min was maintained, the screw conveyor was rotated at 60 rpm, and an addition rate of 0,5 g lignin per min was chosen.

The pyrolysis products were resolved into a pyrolysis residue and ether-soluble and ether-insoluble pyrolyzates. The ether-soluble pyrolyzate was resolved into organic acids, neutral compounds, and phenols. The yields obtained are presented in Table IV.

The phenolic fractions were analyzed by GLC [13], in order to establish the optimum temperature range for receiving a phenolic mixture with a high proportion of low-molecular weight phenols. Two characteristic chromatograms obtained are shown in Figure 3. The further results obtained by gas chromatografic separation of the phenolic fractions are presented in Table V.

DISCUSSION

By preliminary investigations using microscale pyrolysis, it could be shown that the maximum yield of monomeric phenols was obtained by thermal degradation of PL-B, followed by CPL and PL-A (Table II). At the same time the existence of a strong relation between pyrolysis temperature and pyrolysis products formed was detected. Maximum amount of phenols was obtained when the pyrolysis was carried out at temperatures between 400° and 450°C. The yields of solid residue decreased and more uncondensable gas was formed when the pyrolysis temperature was increased.

Microscale pyrolysis of CSLP yielded a mixture of five monomeric phenols in an amount of 30% based on the weight of sodium-free lignin (Table III). Because

of only low-molecular weight compounds like phenol, o-cresol, p-cresol, guajacol and ethyl-phenol were obtained, future preference was given to pyrolysis of sodium lignophenolate rather than free phenol lignin, which was always decomposed to a mixture of more than 10 different phenols.

In the investigations on the applicability of a continuous process for large scale pyrolysis of phenol lignin, results obtained by micropyrolysis of CSLP could be confirmed only qualitatively. The influence of temperature on the amounts of pyrolysis products is evident from Table IV. With increasing temperature, less ether-insoluble pyrolyzate, less neutral compounds, and less organic acids were formed, while the optimum yield of phenolic products was obtained from SLP-A at 600°C. If pyrolysis was carried out at temperatures higher than 650°C, further cracking of the phenols formed was observed.

The phenolic mixtures obtained by continuous pyrolysis were also composed of a maximum of five different phenols (Table V, Fig. 3). In addition, it was observed that the composition of the fraction became less complex when the pyrolysis temperature was increased. If the temperature was higher than 500°C (the upper limit for microscale pyrolysis), no guajacol was detected in the pyrolyzate. Obviously, a removal of methoxyl groups yielded larger amounts of phenol.

The results presented in Tables IV and V show that SLP-A should be pyrolyzed at 600°C in order to afford a maximum yield of a mixture of phenols with a high content of phenol, o-cresol and p-cresol, and only small amounts of ethyl phenol. Evidently, the optimum temperature for the pyrolysis of CSLP is approximately 100°C lower. After the separation of phenol, o-cresol, and p-cresol by distillation from the rest of the ethyl phenol in the phenolic fraction of the pyrolyzate, a mixture of phenols was obtained, which already has been tested as a suitable pulping agent for pine and beech [4].

Until now it was not possible to reproduce the amounts of phenols obtained by microscale pyrolysis of CSLP and make up for the loss of pulping chemicals in the phenol pulping process. However further investigations on the influence of the other process parameters, and the application of larger quantities of test material will probably establish the optimum working conditions for the pyrolysis kiln employed here.

REFERENCES

[1] R. Hartmuth, Germ. Patent 326,705 (1919).

[2] R. Hartmuth, Germ. Patent 328,783 (1919).

[3] W. Schweers and M. Rechy, *Papier, 26,* 585 (1972).

[4] W. Schweers, *Chemtech., 132,* 490 (1974).

[5] K. Kratzl, J. Zauner, and P. Claus, *Holzforschung, 18,* 47 (1964).

[6] F. E. Brauns, *The Chemistry of Lignin,* Academic Press, New York, 1952, p. 479.

[7] F. E. Brauns and D. A. Brauns, *The Chemistry of Lignin,* (Suppl. Vol.), Academic Press, New York, 1960, p. 477.

[8] W. Schweers, H. Behler, and O. Beinhoff, *Holzforschung, 26,* 103 (1972).

[9] W. Schweers, O. Faix, and W. Vorher, *Holzforschung, 25,* 105 (1971).

[10] K. Sarkanen and C. Schuerch, *Anal. Chem, 27,* 1245 (1955).

[11] F. Vieböck and A. Schwappach, *Ber., 63,* 2818 (1930).

[12] J. Marton and T. Marton, *Tappi, 47,* 471 (1964).

[13] W. Schweers, *Holzforschung, 23,* 5 (1969).

[14] D. W. Goheen and J. B. Martin, Can. Patent 791,772 (1968).

PHENOLICS AND OTHER ORGANIC CHEMICALS FROM KRAFT BLACK LIQUORS BY DISPROPORTIONATION AND CRACKING REACTIONS

TERJE ENKVIST*

*University of Helsinki, Helsingfors,
Finland*

SYNOPSIS

By adding sodium hydroxide in amounts of about 18% of the dry matter to softwood kraft black liquor with a dry content of about 55%, then spray drying to a dry content of about 95% and heating continuously for 7 min, strong disproportionation and degradation of the organic matter takes place. The lignin is practically completely demethylated, degraded, and hydrogenated, forming crystalline catechol, 4-methyl and 4-ethyl catechol and some other mononuclear phenols, homoprotocatechuic acid and other phenol carboxylic acids, as well as ether soluble derivatives of catechol with molecular weights of between 350 to 1450. By swift cracking at about 500°C of the last named products and of the phenol carboxylic acids, the yields of catechol and its nearest homologs can be more than doubled, to about 48 kg/metric ton of 90% pulp. Other parts of the organic matter are oxidized to oxalic acid in a yield of about 84 kg/ton of 90% pulp. The alkali used can be regenerated, mainly as crystalline sodium sulfate if sulfuric acid is used for acidification of the reaction mixture. Catechol reacts with formaldehyde as swiftly at 75°C as phenol at 90°C. 4-methyl catechol reacts still more swiftly than catechol. Comparisons are made with products from dry distillation of burning shale (Kukkersite) from Estonia, which gives resorcinol, adipic and other dicarboxylic acids, and aromatic hydrocarbons.

INTRODUCTION

The purpose of our research has been to find as cheap and simple a process as possible by which lignin, especially in the form of the whole matter of kraft black liquor, can be converted into phenolics and other useful products in maximum yields. The task has been somewhat frustrating, as phenols had been manufactured more cheaply and easily by other methods until 1973. At present, in the wake of the oil crisis, the trend is reversed. The price of phenol has risen manyfold, and some phenols, resorcinol for instance, have at times been difficult to obtain altogether, at least in some European countries. In this situation, the manufacture of phenols from a renewable source like wood is attracting renewed interest.

* It is with deep regret that we note the death of Dr. Terje Enkvist on July 15, 1975.

We have studied the manufacture of phenols from wood sources in many ways, including hydrogenation [1] and dry distillation of isolated kraft lignin. Freudenberg and Adam [2] heated lignin carefully in a stream of hydrogen at ordinary pressure, usually in the presence of 4%–12% of catalysts, such as nickel compounds. Spruce hydrochloric acid lignin is claimed to give up to 35% of phenols, such as simple phenol, guaiacol, p-creosol, catechol, isoeugenol etc. It seems questionable, however, whether more condensed and sulfur containing lignins, such as kraft lignin and lignosulfonic acids, would give satisfactory yields of low-molecular weight phenols. An interesting approach has been developed by Goheen [3] in his method of dry distillation of dried kraft black liquor, where the main product is guaiacol, obtained in a yield of about 2%, and other organic distilling oils (8%–10% of the solids).

EXPERIMENTAL

Phenols from the Carbohydrates of Wood

At first some rather peculiar new ways of obtaining phenols from wood products may be mentioned, although they are of mostly theoretical interest. The first is the formation of a series of methoxyl free phenols and enols from sugars such as glucose and galactose, but also from xylose, on heating in dilute sodium hydroxide solution at 100°C and also by heating of spruce wood with kraft white liquor and a mixture of 1,2-propylene glycol and butanone. Figure 1 shows the formulas. This work was begun by me in 1951 [4,5] and completed in Helsingfors by Forsskåhl [6] and Nordman [7], the former partly in collaboration with O. Theander in Uppsala, Sweden. The small amounts of catechol and its derivatives which occur in kraft black liquor [8] can thus originate from carbohydrates and not necessarily from lignin. These phenols and enols possibly cause darkening of pulp and paper.

Degradation of Alkali Lignins by Digestion in Alkaline Solutions

Another curious formation of phenolics from wood sources is that which occurs on digestion of isolated sulfate or soda lignins with sodium hydroxide solution at 170°C [9]. By successive 4-hr heating of isolated, ether-insoluble kraft or soda lignin from spruce wood, about 25% of the lignin is degraded to ether-soluble products, among them acetovanillone and vanillic acid. Ether-insoluble lignin fractions from a 2-step kraft digestion of spruce wood, first at 100°C and then at 167°C, after further successive heatings with a 5% sodium hydroxide solution, gave ether-soluble degradation products in yields of 35% or more. Leopold [10] has shown that acetovanillone can be oxidized to vanillin by heating with nitrobenzene and sodium hydroxide solution.

Heating under Pressure of Kraft Black Liquor with Added Sodium Sulfide

On heating under pressure kraft black liquors with added sodium sulfide at about 250°–280°C, dimethyl sulfide, methyl mercaptan, catechol and catechol derivatives, as well as other products are formed. This process was originally pat-
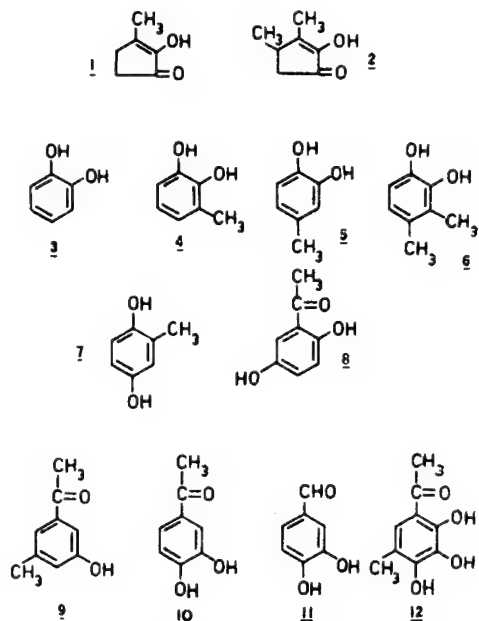
FIG. 1. Formulas of phenols and enols obtained on heating of glucose, xylose, or spruce wood with alkaline solutions [5,6]. Nos. 1, 2, 9, and 10 also from wood.

ented [11] for the manufacture of dimethyl sulfide, which then should be oxidized to dimethyl sulfoxide [12,13]. The patent was taken over by Crown Zellerbach and completed by adding an obvious way to obtain the extra sodium sulfide, namely by addition of sulfur to the black liquor [14]. Later, I and my coworkers in Helsingfors, investigated the demethylated liquors formed in the process and found them to contain considerable amounts of catechol and its homologs and derivatives. We especially studied the yields of ether-soluble phenolic and acidic degradation products on swift, continuous heating and under pressure also on batchwise heating in autoclaves at 250–290°C of kraft and soda black liquors and sulfite spent liquors after additions of sodium sulfide or sodium hydroxide plus sulfur [15–18]. The yields of ether-soluble, nonvolatile matter, which could be extracted after acidification of the reaction mixture, are dependent on the time of heating, and decrease if the time exceeds 5–10 min.

Heating of Kraft Black Liquors at Ordinary Pressure after Addition of Sodium Hydroxide and Spray Drying

Later it was found [19–21] that better yields of ether-solubles and also of catechol and its nearest homologs are obtained when the heating is carried out at ordinary pressure in an atmosphere of nitrogen at about 310°C after addition of sodium hydroxide to kraft black liquor in an amount of about 18% of the solids and spray drying to a content of solids of about 90%. The heating can be carried out continuously (Fig. 2) on a conveyor belt, in about the same fashion as that used for isomerization of phthalate to terephthalate. The optimal heating time is about 7 min. Dimethyl sulfide, water, and small amounts of methanol, ethanol, acetone, cyclopentanone, 2-methyl, 3-methyl and 2,4-dimethyl cyclopentanone, guaiacol,
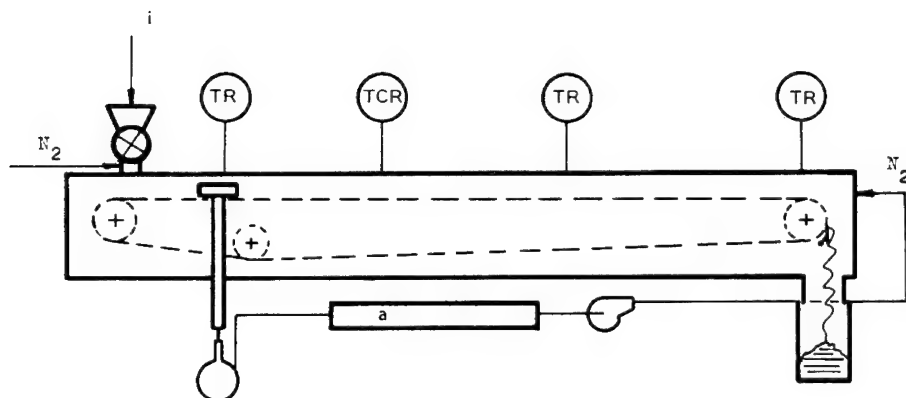
FIG. 2. Principle drawing of continuous reactor. TR and TCR = thermoelements connected with recorders; I = inlet for spray dried black liquor + NaOH; a = absorption carbon.

and probably also phenol, o-, m- and p-cresol, p-ethyl phenol, p-propylphenol and ethyl guaiacol (Table I) distill off during the heating [22,23].   The main product is a brittle, brown powder (DK), easily soluble in water.   In our experiments it has usually been processed by dissolution in water under swift, stepwise neutralization

TABLE I
Organic Substances from Kraft Black Liquors[a]

Kraft black liquor	Original[b]	Na$_2$S-pressure heated	NaOH-heated at ordinary pressure
Nonvolatile substances:			
Water insolubles:			
Ether insolubles (DL)	422	410	55
Ether solubles (ES)	30	66	330[c]
Water solubles:			
Oxalic acid			87
Succinic acid			18
In addition:			
Ether solubles (EWS)	51	77	186[d]
Butanone solubles	85[e]	90	59
Volatile substances:			
Dimethylsulfide	2.3[f,g]		15.0
Methylmercaptan			4.0
Methanol[f]	12.0		2.9
Ethanol and acetone	1.3		2.3
Cyclopentanone and homologs			0.9
Guaiacol and other volatile phenols			3.4
Formic acid	40		85
Acetic acid	46		55
Propionic acid			10

[a] Yields in kg/metric ton of 90% pulp.

[b] After separation of crude soap.

[c] Gives catechols on cracking (Tables III and IV).

[d] Contains catechols and homoprotocatechuic and other phenolcarboxylic acids.   These acids can be cracked to catechols (Table IV).

[e] In addition 230 kg methanol solubles.

[f] Volatile on blowing of digester.

[g] In addition 12 kg of turpentine and 30 kg of crude tall oil.
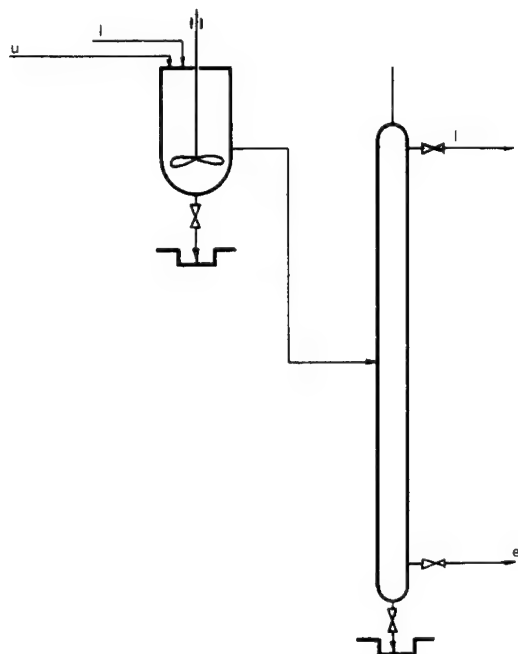
FIG. 3. Principle of countercurrent extractor for extraction of salt solutions with light solvents. l = solvent; u = solution to be extracted; e = water solution after extraction.

and acidification with sulfuric acid or sulfur dioxide concomitant with introduction of steam. The cost of sulfuric acid is the largest single item among the cost for chemicals. Diluted waste acid can be used. Carbon dioxide is less suitable.

Phenols and most of the acids have usually been extracted with ethyl acetate, to which some alcohol has been added. Acidic sodium oxalate crystallizes from the water layer. The alkali is recovered, for the most part as crystalline sodium sulfate, the rest being added in solution to the recovery system of the kraft mill. Catechol can be distilled with superheated steam. The sludge, which is precipitated on acidification, tenaciously retains water-soluble products such as simple phenols and sodium oxalate. Hence, it has usually been washed with small amounts of water or aqueous solutions concomitant with introduction of steam of 100°C. It has been suggested [24] that the total aromatic material be removed by centrifugation. Under these circumstances it will also contain the oxalates, and we have therefore preferred to use solvents like ethyl acetate. A simple countercurrent extractor (Fig. 3) was constructed and functioned well.

Table I gives the yields of the main fractions and products and also includes a comparison with the yields of corresponding fractions from original kraft black liquor and from kraft liquor heated with sodium sulfide under pressure. Not only the yields but also the compositions of the fractions are much inferior to those obtained on heating with sodium hydroxide. That carbohydrates, as has been shown, can be changed to phenols is to be considered in explaining the fact that the yield of the ether-soluble fractions EWS and ES can be larger than the amount of the lignin in the original kraft black liquor.

Sodium-base sulfate spent liquors from digestions of softwoods can be used instead of kraft black liquors, but they require addition of greater amounts of sodi-
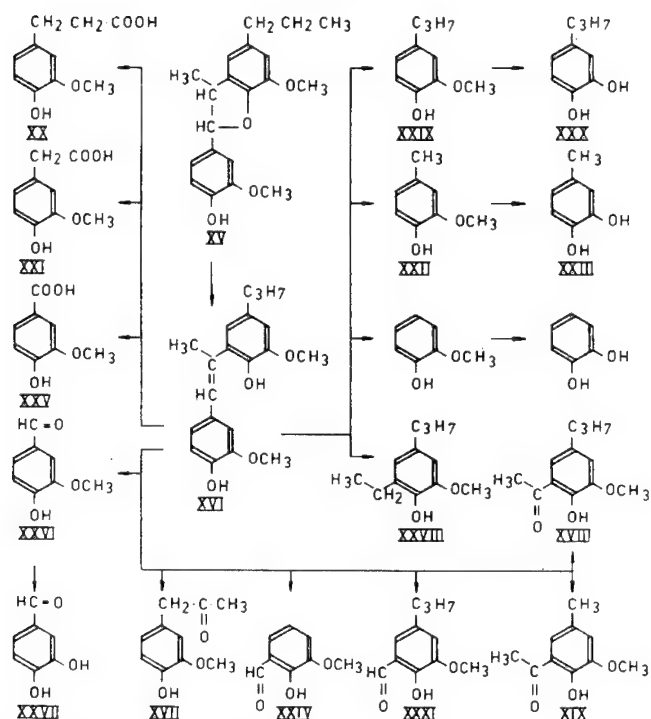
FIG. 4. Degradation of the lignin model dehydro-di-isoeugenol on heating with sodium hydroxide [25].

um hydroxide than kraft black liquors. Black liquors from hardwoods have also been used. They give, of course, lower yields of catechol and its homologs. Instead, pyrogallol and its derivatives are formed, but they are so easily autoxidized, that they are difficult to isolate. Soda black liquors from digestions of softwood should theoretically give more pure reaction products than kraft black liquors, but we do not have any such industry in Finland.

The main reactions on heating with sodium hydroxide of the spray-dried liquor at ordinary pressure are rather different from those obtained on heating of kraft black liquor with sodium sulfide under pressure. At ordinary pressure, the reactions are comparable with those prevailing on ordinary alkali melting, even if the amount of sodium hydroxide used is small, in fact about half of the amount of alkali used on kraft digestion of the corresponding amount of wood. As in other alkali meltings, the presence of some water, about 10%, is indispensable.

The methyl groups are practically completely removed. Model experiments (Fig. 4) [25,26] suggest that cleavage, not only of ether bonds but also of carbon-carbon bonds, occurs to a great extent, causing degradation to low molecular products. Elementary analyses of fractions of the ether-soluble, water insoluble fraction (ES) show that the lignin has been strongly hydrogenated (Table II, cf. also Fig. 5). As on the other hand large amounts of sodium oxalate are formed, strong disproportionation reactions clearly take place. The role of the nonlignin organic matter, and a part of the lignin in the black liquor at the disproportionation, is very probably to hydrogenate the lignin and itself be oxidized to oxalic acid and other carboxylic acids, including phenol carboxylic acids. Among them homoprotocatechuic acid dominates.

That the presence of organic matter to be oxidized is necessary for the degradation and hydrogenation reactions could be seen in experiments, where isolated kraft lignin was heated with sodium hydroxide at ordinary pressure in steel tubes.
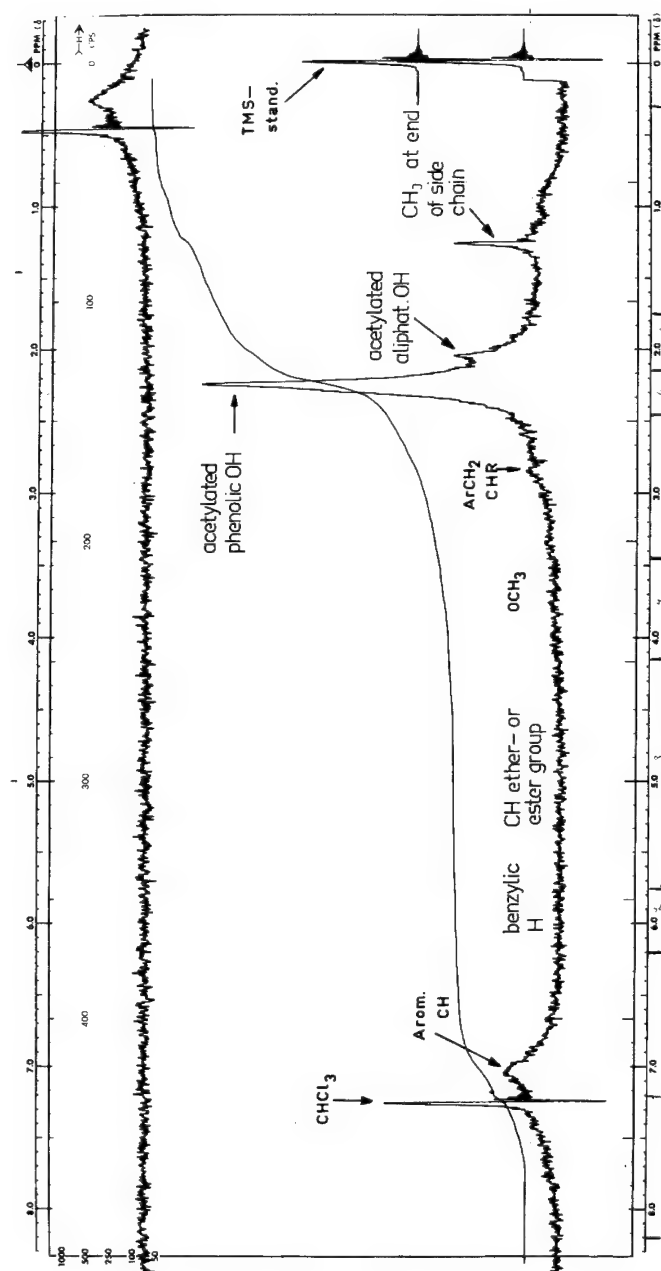
FIG. 5. NMR-spectrum of ES-fraction.

TABLE II

Composition of the Ether-Soluble (ES) and Ether-Insoluble (DL) Nonvolatile and
Water-Insoluble Fractions from Demethylated Black Liquor (DK)

Fraction	Yield, % of ES	Empiric formula for C_9-unit	Hydrogenation formula No	Molecul. weight, osmometry	Aromatic IR-absorption cm⁻¹	
					1600	1510
Butanone [a]	6,3	$C_9H_9O_{3,5}$	-	1200	+	-
DL	20	$C_9H_{8,5}O_{2,9}$	1			
F I [b]		$C_9H_{9,3}O_{2,75}$	2	1213		
S I [c]		$C_9H_{10}O_3$	3			
Eth.ac. [d]	10,8	$C_9H_{9,5}O_{2,5}$	4	970	+	(+)
F II b [d]		$C_9H_{9,75}O_{2,6}$	5			
Ether sol. [d]	30,3	$C_9H_9O_2$	6	639	++	+
i-amylacet. [d]	19,1	$C_9H_{10}O_2$	7	862 [e]	+	(+)
S II [f]		$C_9H_{10}O_3$	3	380		
F III [d]		$C_9H_{11}O_2$	8	350		
CHCl₃-sol. [d]	1,4	$C_9H_{11,5}O_2$	9	1450	++	+
CH₂Cl₂-sol. [d]	26,5	$C_9H_{11,5}O_2$	9	g	++	(+)
petrol eth. [d]	0,6	$C_9H_{12,5}O_{1,75}$	10		++	+
toluene sol. [d]	0,4	$C_9H_{13,5}O_{1,5}$	11		+	++

[a] Butanone-soluble fraction from successive solvent fractionation of ES.
[b] A phenolic fraction from ES.
[c] An acidic fraction of ES.
[d] Fraction from successive solvent fractionation of ES.
[e] 3.8% of C-methyl.
[f] Another acidic fraction from ES.
[g] 7.0% of C-methyl.

Table IIa
Hydrogenation Formulas Corresponding to Table II

No	
1	$C_9H_9O_{3,5} - 0,7\ H = C_9H_{8,5}O_{2,9} + 0,6\ H_2O$
2	" $+ 1,8\ H = C_9H_{9,3}O_{2,75} + 0,75$ "
3	" $+ 2\ H = C_9H_{10}O_3 + 0,5$ "
4	" $+ 2,5\ H = C_9H_{9,5}O_{2,5} + 1$ "
5	" $+ 2,55\ H = C_9H_{9,75}O_{2,6} + 0,9$ "
6	" $+ 3\ H = C_9H_9O_2 + 1,5$ "
7	" $+ 4\ H = C_9H_{10}O_2 + 1,5$ "
8	" $+ 5\ H = C_9H_{11}O_2 + 1,5$ "
9	" $+ 5,5\ H = C_9H_{11,5}O_2 + 1,5$ "
10	" $+ 7\ H = C_9H_{12,5}O_{1,75} + 1,75$ "
11	" $+ 8\ H = C_9H_{13}O_{1,5} + 2$ "

The resulting yields of ether-soluble fractions after acidification (EWS and ES, Table I) was about the same when calculated on the amount of the kraft lignin used as starting material, as were the corresponding yields from heating of kraft black liquor, calculated on the entire organic matter of the black liquor.

The large ES-fraction is soluble in neutral sodium molybdate solution and can, to a great extent, be cracked at about 500°C to a very similar mixture (Table III) of catechol, methyl catechol, and ethyl catechol as that which is found in the fraction (EWS) which after acidification is soluble in water and ethyl ether. The ES

TABLE III
Example of Composition of Cracking Distillate from The ES-Fraction

	Yields		
Cracking distillate	44.9 % of ES		
Catechol	7.1 %	"	distillate
4-methyl catechol	6.0 %	"	"
4-ethyl catechol	3.2 %	"	"
Phenol	1.2	"	"
Cresols	1.2	"	"
4-ethyl-phenol	+		

thus consists mainly of catechol derivatives. Further yields of the same mixture of catechol and its homologs can be obtained by cracking of the water-soluble phenol carboxylic acids (Table IV).

The crackings have been carried out as flash crackings in a quartz vessel heated in a metal bath. The technique developed should be of interest for analysis of other chemical substances. The yields were determined by gas chromatography. The catechol can be easily isolated in a chromatographically pure state by simple crystallization of the mixture with its homologs from benzene. On a commercial scale, distillation or sublimation should be considered.

If the crackings in the quartz vessel are carried out at about 800°C, the distillate contains mainly monovalent phenols, such as phenol and its homologs, cresols, xylenols, etc. Small amounts of such monovalent phenols are found also in the catechol-containing distillates obtained on cracking of the ES-fraction at about 500°C (Table III).

The combined yields of catechol and its simple homologs can amount to about 48 kg/ton of 90% pulp (see Table IV), thus exceeding the yield of the tall oil. Besides catechol and the alkyl catechols, small amounts of 4-acetocatechol, protocatechualdehyde, resorcinol and its homolog orcinol are also formed.

Succinic acid precipitates during the evaporation of the ethyl acetate extracts. Homologs of succinic acid are also formed, such as glutaric and adipic acid, albeit in low yields.

Formic and acetic acid already occur in the original black liquor, but they increase in amount on heating with alkali, which also generates some propionic acid (Table I). As a source of acetic acid, the process can hardly compete with the acidification and distillation of spent liquors from high-yield pulping of hard-

TABLE IV
Yields of Catechol and Homologues in kg/ton of 90% pulp

		catechol	catechol	
Directly from EWS	9	6	6	21
In addition from cracking of ES	7	5	4	16
In addition from cracking of carbo-xylic acids from EWS	5	4	2	11
Total	21	15	12	48

woods. The mixture of acetic and formic acids could be used for preservation of cattle fodder. The mixture could also be esterified with ethanol or other simple alcohols, thus producing, for instance, the solvents needed for extraction of the reaction products. It does not seem impossible that esters of lactic acid could also be prepared in this way from fractions of the reaction mixture. If pure formic acid is desirable, it could be produced by known methods from the abundant oxalic acid. Oxalic acid could also be used for manufacture of oxalyl chloride with the aid of thionyl chloride. Oxalyl chloride can for some purposes replace phosgene. Owing to its higher boiling point, oxalyl chloride should be less dangerous than phosgene.

Comparison with Estonian Shale Oil

It can be of interest to compare the heating of black liquor with the somewhat similar dry distillation of Estonian oil shale (Kukkersite). This shale contains about 60% of organic matter, more than many other oil shales. Through intense research carried out after the war [28,29] it has been found that the Estonian shale gives high yields of a variety of useful products, namely toluene and other aromatic hydrocarbons, resorcinol, the most valuable of the simple bivalent phenols, and further, through oxidation of the kerosene fraction, a mixture of adipic acid, and other dicarboxylic acids. This mixture can be esterified and used as plasticizer. The resorcinol is used for manufacture of adhesives and possibly also of styphnic acid (2,4,6-trinitroresorcinol).

Uses of Catechol

We have studied the use of catechol, its homologs and also the EWS- and ES-fractions as starting materials for the manufacture of adhesives for plywood and wallboard. In addition to numerous adhesive preparations and testings, the reaction between catechol and formaldehyde has been studied with the aid of paper and thin layer chromatography and ultraviolet spectroscopy. Catechol reacts with formaldehyde about as rapidly at 75°C as phenol at 90°C, and 4-methyl catechol reacts still faster. The ultraviolet spectra indicate that the reaction of catechol with formaldehyde is strongly dependent on pH, the flattening out of the minimum of the absorption curve having a maximum velocity at a pH of about 9, a minimum at pH 11 and another maximum above a pH of 12.

It has been maintained that addition of limited amounts of catechol or of its homologs to common phenol would be of advantage for the preparation of adhesives by reaction with formaldehyde [29].

It appears that catechol is now manufactured by Crown Zellerbach, and this firm has sent out reviews of possible uses [30,31]. One of these is the hydrogenation to 1,2-cyclohexanediol, which like cyclohexanol can be oxidized to adipic acid [35]. It would be very interesting to isomerize catechol to resorcinol. This should be possible, in principle, via a benzene derivative [33].

DISCUSSION

The heating of black liquor with alkali in the manner outlined gives a variety of products, whose value, if all of them could be sold, should exceed the value of the

corresponding amount of pulp. A disadvantage of the process is, of course, that the products are numerous and that their separation, and also the cracking processes still offer problems, as does also the marketing of so many products by one manufacturer. The separation of the products is, however, simple in principle, and the difficulties should not be unsurmountable by modern methods of automation.

Catechol and its derivatives are swiftly autoxidized in alkaline solution, but this difficulty can easily be overcome by swift neutralization during the dissolution of the residue of the heating in the continuous reactor. Cracking processes have been marvellously developed in the petroleum industry. It seems probable that they could be perfected in a similar way for the black liquor process described in the present paper, if they were studied in only a minute proportion of the amount of research which has been carried out in the petroleum industry.

REFERENCES

[1] T. Enkvist and J. Halmekoski, *Suom. kemistilehti B, 29*, 53 (1956).
[2] K. Freudenberg and U. K. Adam, *Chem. Ber., 74*, 387 (1941).
[3] D. W. Goheen, U.S. patent 3,375,283.
[4] T. Enkvist, *Acta Chem. Scand., 8*, 51 (1954).
[5] T. Enkvist, *Finska kemistsamf. medd., 71*, 104 (1962).
[6] I. Forsskåhl, Licentiate Thesis, University of Helsinki, 1972.
[7] G. Nordman, Licentiate Thesis, University of Helsinki, 1970.
[8] T. Enkvist, J. Turunen, and Th. Ashorn, *Tappi, 45*, 128 (1962).
[9] T. Enkvist and B. Alfredsson, *Tappi, 36*, 211 (1953).
[10] K. V. Sarkanen and C. H. Ludwig, *Lignins,* Wiley-Interscience, New York, 1971, p. 438.
[11] E. Hägglund and T. Enkvist, U.S. patent 2,711,430 (1955).
[12] T. Smedslund, Swed. patent 121,576; *Chem. Abstr., 43*, 3438 (1949).
[13] G. Wetterholm and K. Fossan, U.S. patent 2,702,824 (1955).
[14] M. E. Cisney and D. W. Goheen, U.S. patent 2,908,716 (1959).
[15] T. Enkvist, B. Holm, J. Turunen, and K. Turunen, *Finska kemistsamf. medd., 70*, 1 (1961).
[16] T. Enkvist, *Svensk kem. tidskr., 72*, 93 (1960).
[17] T. Enkvist, E. Manelius, and B. Yrjas, *Finska kemistsamf. medd., 76*, 102 (1967).
[18] T. Enkvist, J. Turunen, and K. Turunen, *Finska kemistsamf. medd., 76*, 94 (1967).
[19] T. Enkvist and T. Lindfors, *Finska kemistsamf. medd., 75*, 1 (1966).
[20] T. Enkvist and T. Lindfors, *Paper and Timber, 48*, 639 (1966).
[21] T. Enkvist, *Kemisti, 13*, 7 (1967).
[22] Ö. Wahlroos and T. Enkvist, *Acta Chem. Scand., 22*, 3202 (1968).
[23] T. Enkvist, *Kem. teollisuus, 26*, 619 (1969).
[24] K. Sarkanen and C. H. Ludwig, *Lignins,* Wiley-Interscience, New York, 1971, p. 591.
[25] J. Turunen, *Soc. Scient. Fenn. Comm. Phys. math., 28*, (1963).
[26] T. Enkvist, Symp. Internat. de Grenoble, Chim. de la lignine etc., 177 (1964).
[27] T. Enkvist, *Kem. teoll., 28*, 736 (1971).
[28] A. Aarna, Pölevikeemia probleeme Eesti NSV-S, Eesti Raamat. Tallinn (1965).
[29] A. Aarna, Esti NSV Teadust. Akad. toimetuks. Füüs. Mat. ja Tekn. (1964).
[30] G. E. Throughton, J. F. Manville, and S. Z. Chow, *Forest Prod. J., 22*, 108 (1972).
[31] G. E. Throughton, *Holzforschung, 26*, 170 (1972).
[32] H. G. Freeman, G. F. Baxter, and G. G. Allan, U.S. patent 3,518,159 (1970).
[33] Crown Zellerbach Corp., Camas, Washington, "Applications for catechol," 1973.
[34] Crown Zellerbach Corp. Camas, Washington, "Reactions of catechol," 1974.
[35] K. Kratzl, *Österr. Chem. Zeit., 62*, 102 (1961).

POLYURETHANE FOAMS FROM CARBOXYLATED LIGNINS

OSCAR H.-H. HSU and WOLFGANG G. GLASSER

Department of Forestry and Forest Products,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061

SYNOPSIS

Softwood lignin from a kraft pulping black liquor has been converted into a polyol suited for the preparation of semirigid polyurethane foams by modification with maleic anhydride and alkylene oxides. Carboxylation was carried out in an autoclave at 170°C for 2 hr. The reaction, which was followed by hydrolysis, involves esterification and free-radical vinyl copolymerization to yield a copolymer with 10 acid meq/g. Oxyalkylation with propylene oxide afforded a viscous, dark brown polyester-polyether-polyol with a hydroxyl number of 420. This polyol was subsequently reacted with various diisocyanates in the presence of water or freon to yield polyurethane foams of low density. When compared to oxyalkylated kraft lignin it was found that the lignin polycarboxylic acid reacted more completely with propylene oxide, and, with toluyl-di-isocyanates, generated foams more uniform in cell structure and with a higher strength and lower density. The results suggest that lignin may become a versatile and competitive polyol through modification with maleic anhydride and alkylene oxides.

INTRODUCTION

Lignin is recognized as a three-dimensional, highly branched polymer which contains a variety of functional groups, and which is capable of a large number of modification reactions. Hydroxyl groups, both aliphatic and aromatic, are abundant and offer easy modification sites. Because of this multifunctionality, lignin can be considered a natural polyol with some potential for preparation of polyurethanes.

Moorer, Dougherty, and Ball [1] have recently employed lignin in the formation of polyurethane foams by dissolving lignin in glycols and then reacting it with diisocyanates. The reaction was described as the isocyanate acting as a bridge substance linking the two kinds of polyol. The hydroxyl groups in lignin were assumed to be the key in this reaction. Attempts to reveal details of the reaction mechanism of lignin with isocyanates have been undertaken by Kratzl and coworkers [2], and Yaunzems and coworkers [3]. In a series of experiments, the reactivity of model compounds containing various functional groups with mono- and

297

diisocyanates were investigated. The results were discouraging, which was attributed to a paucity of reactive positions. More recently, attempts were made by Christian and coworkers [4] to increase the number of reactive positions in lignin by condensation with ethylene oxide, propylene oxide, and an alkyl sulfide. The reactions were shown to produce oils with viscosities and hydroxyl numbers suitable for mixing and reacting with diisocyanates in the formation of rigid polyurethane foams. High rigidity, high water absorption, and low strength appear to be the main drawbacks of the resulting oxyalkylated lignin-urethane foams. Ishikawa, Oki, and Fugita [5] observed that phenolic hydroxyl groups of lignin model compounds react quantitatively with ethylene oxide if the sidechains do not contain carbonyl groups or other unsaturated moieties. Phenolic hydroxyl groups of model compounds with unsaturation in the sidechains exhibited great resistance to hydroxyl-ethylation. It must therefore be expected that the obstruction of conjugated systems, the conversion of phenolic hydroxyl groups to aliphatic ones, and the incidental introduction of long chains of aliphatic alcohols, carboxylic acids or esters, will render the lignin macromolecule a useful and versatile polyol for the preparation of polyurethane foams [6]. The objective of this study was to demonstrate the versatility of lignin as a coreactant in polyurethane formation by reducing the unsaturation of lignin by reacting it with maleic anhydride via a vinyl-type copolymerization, and, at the same time, to add carboxyl groups and to activate phenolic hydroxyl groups for later oxyalkylation.

EXPERIMENTAL

Modification Reactions

Lignin-Maleic Anhydride Copolymerization

Two parts of kraft lignin (Indulin AT by Westvaco Corp., Charleston, South Carolina) were completely mixed with 1 part of maleic anhydride, and this mixture was placed in a glass tube which was sealed and placed in a stainless steel autoclave, where it was kept for 2 hr at 170°C. After cooling and carefully relieving the pressure of the autoclave, the copolymer was removed from the reaction vessel. It was ground into a fine powder, washed with ether to remove the excess maleic anhydride, and air dried.

Saponification

Fifteen g of the copolymer were transferred to a reaction flask and completely dissolved in 1400 ml of 2 N aqueous NaOH. After refluxing this solution under a steady stream of N_2 for 1 hr, the dissolved black solution was cooled to room temperature and the copolymer precipitated by acidification with 1 N sulfuric acid. The precipitate was centrifuged at 9000 rpm for 20 min, and washed with distilled water twice, and with very dilute (0.01 N) HCl solution three times. Care was exercised at this stage to prevent loss of any solubilized carboxylated lignin. The completely washed, inorganic-free substance was then freeze dried.

Oxyalkylation Reaction

One part of the dried copolymer, 10 parts propylene oxide and 1% KOH catalyst, were sealed inside a reactor. The mixture was agitated and heated to maintain 170 psi pressure and 140°C for 2 hr. After about 1 hr the polymerization started, which was signalled by the pressure dropping and the temperature rising. When the pressure had dropped to zero, or some specific point depending on the desired D.P., a black, viscous material was obtained. The removal of excess propylene oxide was accomplished by vacuum evaporation. The resulting material was dissolved in methanol, and inorganic substances were removed by adding tartaric acid. Evaporation of the filtrate was performed under reduced pressure at 80°C to remove the methanol. The resulting substance is a lignin polyester-polyether polyol.

Polyurethane Foam Formation

A polyurethane foam was prepared from the formulation listed in Table I. The amount of isocyanate added to this mixture was calculated on the basis of the total concentration of hydroxyl and carboxyl groups of the polyol and water. The 110 index corresponds to a 10% excess of isocyanate over the amount required by stoichiometry. The mixture was agitated vigorously for about 10–15 sec after which it was allowed to rise. Other foams were obtained by similar procedures using freon as blowing agent and additional chemical modifiers, such as castor oil, glycols, and others.

TABLE I
Formulation of a Polyurethane Foam

Reactants	Parts in Grams
Polyester-polyether polyol	100
Water	1.5
L-520[a]	1.5
Union Carbide A-1 catalyst	0.2
Union Carbide T-9 catalyst	0.3
Isocyanate	110 (index)

[a] surfactant.

Analytical Methods and Procedures

Methoxyl. The procedure followed Tappi Standard T2M-60. Prior to each determination, the apparatus was calibrated with purified vanillin.

Acid Groups. Potentiometric titrations were performed with a Fisher Accumet Model 230 pH meter; 0.01 N NaOH was used as titrant; dimethylformamide-water served as solvent.

Conductometric titrations were carried out using the method of Sarkanen and Schuerch [7]. The samples were dissolved in DMF and water and titrated with

0.1 N NaOH. An Industrial Instrument conductivity bridge, Barnstead Model PU-70CB, was used in conjunction with a Beckman conductivity cell.

Hydroxyl Numbers [8]. Hydroxyl numbers were obtained by esterification with acetic anhydride and pyridine and subsequent back-titration of the excess anhydride with standard base (0.1 N NaOH).

$$\text{OH number} = \frac{56.1 \times \text{N NaOH} \times (\text{ml blank-ml sample})}{\text{sample weight}}$$

Acid Numbers [8]. Samples were dissolved in a 1:1:1 mixture of benzene, isopropyl alcohol, and methanol, and the resulting single phase solution was titrated with standard 0.1 N alcoholic KOH.

$$\text{acid no.} = \frac{\text{ml KOH for sample-ml KOH for blank}}{\text{sample weight}} \times \text{N KOH} \times 56.1$$

Infrared. Infrared spectra were obtained with KBr pellets with a mixing ratio of 1:50 on a Perkin-Elmer Model 62 IR spectrometer.

Compression Strength. The procedure of ASTM standard D695 was followed.

Water Absorption. The procedure of ASTM standard D570 was followed, except that the material was subjected to a saturated atmosphere at 23°C for 2 months.

Viscosity. A capillary viscometer was used, and methanol served as solvent.

RESULTS AND DISCUSSION

Carboxylation of lignin in wood with maleic anhydride has previously been explored by Sandermann and coworkers [9,10] in a reaction aimed at delignification. It was reported that poplar wood gave a pulp with almost no residual lignin when
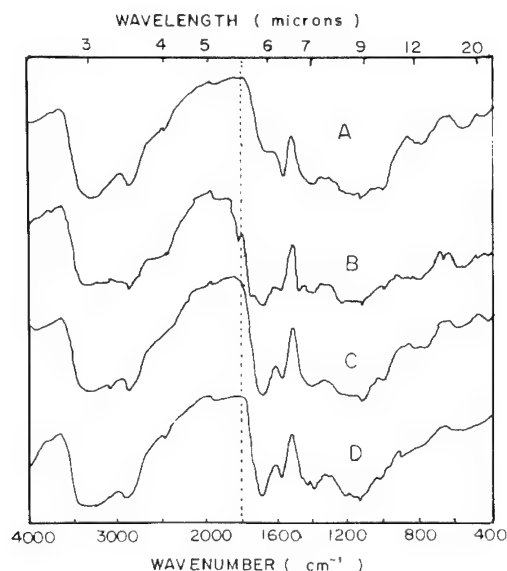
FIG. 1. (A) IR spectra of kraft lignin. (B) Lignin-maleic anhydride copolymer. (C) Hydrolyzed copolymer. (D) Hydrolyzed and reduced copolymer.
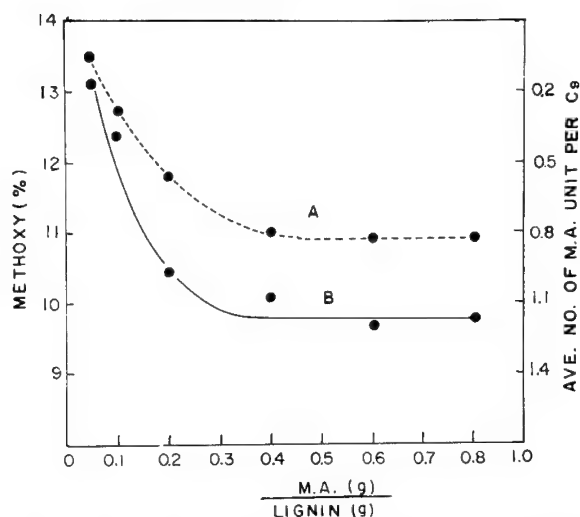
FIG. 2. Relationship between lignin-maleic anhydride mixing ratio and methoxyl content and maleic acid uptake. (A) Hydrolyzed copolymer. (B) Unhydrolyzed copolymer.

it was treated with maleic anhydride at 170°C in an autoclave and saponified with sodium hydroxide. In contrast, no delignification was accomplished when succinic anhydride was used. These results indicated that lignin reacted with maleic anhydride to form a nonhydrolyzable copolymer. Glasser and Sandermann [11,12], working with lignin model compounds, found that styrene derivatives with different substituents are capable of copolymerizing with maleic anhydride. These authors also demonstrated that lignin model compounds without vinyl groups also participate in the copolymerization. The reaction was described as proceeding via intermediary formation of vinyl groups or via a free radical pathway.

The adoption of a similar reaction procedure to kraft lignin afforded a product, the IR spectrum of which is shown in Figure 1. A comparison of spectra of lignin
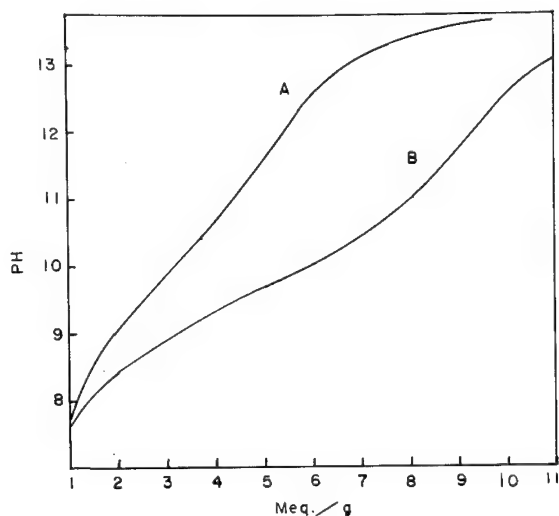
FIG. 3. Potentiometric titration curve of kraft lignin and carboxylated kraft lignin. (A) Kraft lignin. (B) Carboxylated kraft lignin.
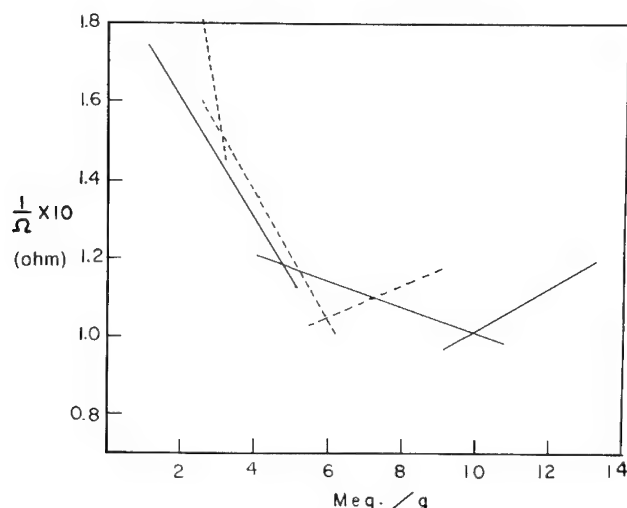
FIG. 4. Conductometric titration curve of kraft lignin and carboxylated kraft lignin. (- - - -) Kraft lignin. (—) Carboxylated kraft lignin.

samples before and after reaction with maleic anhydride, after saponification, and after borohydride reduction reveals that the increase of bands at 1700–1720 cm^{-1} reflects the formation of carbonyl and carboxyl groups in the maleic anhydride treated lignin.   Bands at 3400 cm^{-1} and at 2900–2950 cm^{-1} represent increases in bound hydroxyl, and CH in saturated aliphatic structures, respectively.   Borohydride reduction eliminates the contributing effect of carbonyl groups to the 1700–1720 band by converting keto and aldehyde groups into hydroxyls.   The IR spectrum of the resulting material still indicates the presence of high concentrations of carboxyl groups in the lignin-maleic anhydride copolymer.   This provides conclusive evidence for the incorporation of maleic anhydride molecules into kraft lignin by C-C-covalent bonds.

The extent to which maleic anhydride units are grafted onto lignin was assessed by methoxyl content determinations and by conductometric and potentiometric ti-
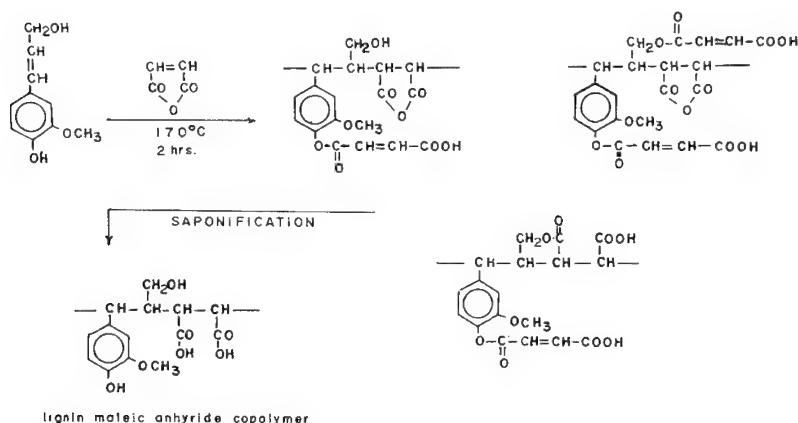
FIG. 5. Probable reaction mechanism for the reaction between lignin and maleic anhydride, illustrated with coniferyl alcohol.
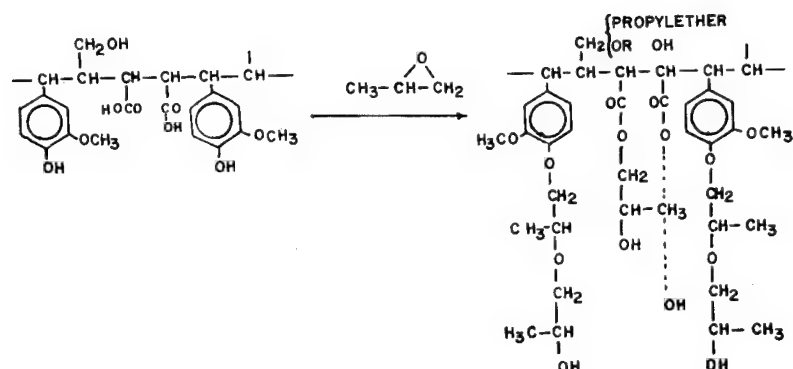
FIG. 6. Reaction scheme for the reaction of carboxylated lignin with propylene oxide.

trations. The relationship between methoxyl content, maleic acid-uptake, and the lignin-maleic anhydride mixing ratio is depicted in Figure 2. The methoxyl contents of the copolymers decline with increasing anhydride concentration in the reaction mixture. At a ratio of 5 parts of lignin to 2 parts of maleic anhydride the curve starts to level off with the resulting copolymer containing 1.2 mol of maleic anhydride per C_9 structural unit of lignin. Following saponification, this number decreases to 0.8 mol or, on the average, about 1.6 carboxyl groups per C_9. The rest was apparently attached to lignin solely via ester linkages. Results of potentiometric and conductometric titrations are given in Figures 3 and 4. Although these results seem to agree with the findings from the methoxyl determinations, it must be recognized that they are more ambiguous due to the difficulties in accu-

TABLE II

Comparison of Physical Properties of Polyols from Kraft Lignin and Carboxylated Kraft Lignin

	Kraft Lignin Polyol	Carboxylated Kraft Lignin
Viscosity	220 cp.	438 cp.
Solubility		
Methanol	V (clear)	V (clear)
DMF	S	V
Ether	I	S (cloudy)
Acetone	S (cloudy)	S (clear)
Benzene	S (cloudy)	S (clear)
Carbon tetrachloride	SS	S
Chloroform	V	V
Toluene	SS	V
Ethyl acetate	I	S (cloudy)
Propyleneglycol	V	V
Dioxane	V (clear)	V (cloudy)
H_2O	S	I
Color	(amber) brown	yellow (brown)
Hydroxyl number	560	420
Carboxyl number	0	0.163 meq/g

V: very soluble
S: soluble
SS: slightly soluble
I: insoluble
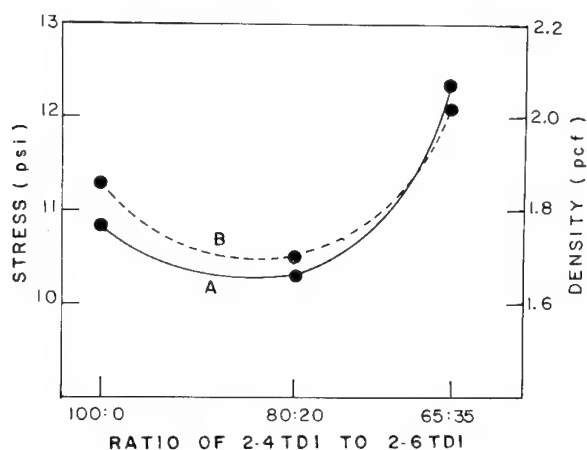
FIG. 7. Relationship between 2,4- and 2,6-toluene diisocyanate mixing ratio and foam strength and density (carboxylated lignin polyol only). (A) Compressive strength. (B) Density.

rately identifying equivalence points. The wide spectrum of ionization constants of the various phenolic, enolic, and carboxylic substituents seems to be the main reason for this phenomenon.

A probable reaction mechanism for the copolymerization reaction is shown in Figure 5. Phenolic phenylalkane units react with maleic anhydride to form half-esters which prevent the abstraction of vinyl radicals by phenolic hydroxyl groups. Vinylic π electrons are then readily activated under the reaction conditions to initiate free radical polymerization with maleic anhydride. Anhydride and ester bonds are subsequently hydrolyzed to yield a lignin-maleic acid chain-copolymer. The carboxyl and phenolic hydroxyl groups of this copolymer offer reactive sites for oxyalkylation to a polyol.

Figure 6 represents the possible reaction scheme of the oxyalkylation. Epoxide ring cleavage of the propylene oxide, initiated by the presence of an alkali catalyst, leads to esterification of carboxyl and etherification of phenolic and aliphatic hy-
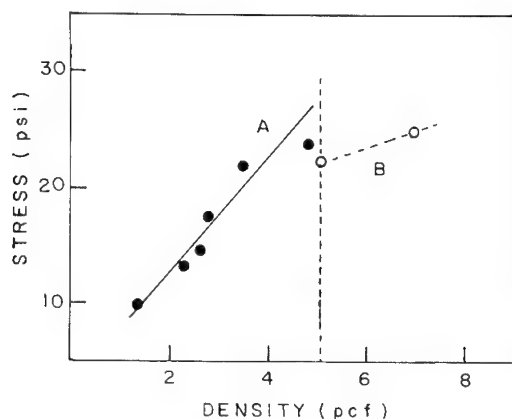
FIG. 8. Relationship between density and compressive strength of foams made from carboxylated and uncarboxylated lignin polyols and TDI. (A) Carboxylated lignin foam. (B) Uncarboxylated lignin foam.

droxyl groups. This reaction produces a highly viscous, homogeneous lignin-based polyester-polyether polyol with properties summarized in Table II. This table also contains a comparison of the carboxylated and oxyalkylated lignin with the merely oxyalkylated product. The data show that the polyol made from carboxylated kraft lignin has a higher viscosity than that from the kraft lignin alone, indicating an increase in molecular weight and a possible lengthening of the branch chains. Both products are soluble in methanol, but the kraft lignin polyol has a higher solubility in water and a lower solubility in ethyl acetate than its carboxylated counterpart. The good solubility of the polyester-polyether polyol in ethyl acetate is a further indication of the influence of the ester linkages of the carboxylated material on the physical properties of this polyol. The two products had hydroxyl numbers of 420 and 560. The lower hydroxyl number of the polyester-polyether polyol demonstrates the effect of an increase in molecular weight which tends to reflect in a lower OH number. The effect of the molecular weight increase is counterbalanced by a higher concentration of carboxyl groups in the modified kraft lignin which causes the hydroxyl number to rise. Apparently, some carboxyl groups survived the reaction with propylene oxide, as some were found in the oxyalkylated end product.

Oxyalkylation converts kraft lignin into an active polyfunctional polyol suitable for mixing and reaction with diisocyanates. Urethane foams were prepared from lignin polyols and mixtures of 2,4- and 2,6-toluyl-diisocyanates (TDI) with water or freon as blowing agents. Isocyanate combination and blowing agent were both found to affect foam rigidity and other physical characteristics. Figure 7 shows the influence of mixing ratio of 2,4- and 2,6-TDI on the strength properties of the resulting foams. Foams made with 80% 2,4- and 20% 2,6-TDI yielded products with lower density and lower elastic modulus than those made with other mixtures. If water was used as a blowing agent, foams with open cell structure, low density, and low modulus were obtained, while freon favored closed cell foams with high modulus which means low flexibility.

TABLE III
Comparison of Properties of Foams from Different Sources (based on 80% 2,4- and 20% 2,6-toluyl-diisocynate)

	Foam From Kraft Lignin Polyol	Foam From Carboxylated Lignin Polyol	Commercial Foam[a]
Compression strength[b]	11.40	22.7 psi	17 psi
% of recovery[c]	0	90%	80%
Water absorption[d]	16.2%	9.7%	
Modulus of elasticity	530.8 psi	380.4 psi	
Density (lbs/ft^3)	6.10	2.54	2.54
Cell structure	collapsed	uniform	
Color	brown	yellow	

[a] data from [13].
[b] based on 20% deflection at 23°C.
[c] following 50% compressive deflection.
[d] after subjection to saturated humidity at 23°C for 2 months.

Figure 8 depicts the relationship between density and strength of foams made with carboxylated and uncarboxylated kraft lignin polyols. The polyester-poly-ether polyol was capable of generating foams with densities as low as 1.64 lb/ft^3. In contrast, foams from uncarboxylated polyols were always found to collapse at densities below about 5 lb/ft^3. At comparable densities carboxylated foams exhibited superior strength properties as compared to their unmodified counterparts (22.7 psi to 17 psi for commercial foam based on the same density).

Results of physical test measurements of foams prepared from oxyalkylated lignin and carboxylated and oxyalkylated lignin are compiled in Table III. The semi-rigid foams made by following the formulation listed in Table I had 90% and 0% recovery after 50% deflection when modified and unmodified lignin was used, respectively. The modulus of elasticity of the foam from the polyester-polyether polyol was low (380.4 psi to 530.8 psi for the foam from kraft lignin polyol), prob-ably due to the influence of the flexible polyether branches. Water absorption was 9.7%, indicating that most hydrophilic hydroxyl groups had reacted with iso-cyanide groups. The polyester foam had a uniform cell structure which can be at-tributed either to a uniform distribution of functional groups, or to uniform reac-tion rates of functional groups, or both.

An additional benefit of carboxylation results from the elimination of chromo-phoric double bonds in kraft lignin during vinyl copolymerization. While kraft lignin has a typical dark brown appearance, carboxylated lignin is only pale yel-low. This difference in color is also apparent in the finished foam.

A general comparison of polyurethane foams made with different formulations from different polyols is difficult to perform and results may be misleading; too many variables are involved, and optimum conditions vary from one polyol to an-other. However, it is safe to conclude the carboxylation with maleic anhydride followed by oxyalkylation offers a combination of modification reactions that lead to polyols and urethanes, the physical properties of which can be well controlled within wide margins. This versatility, however, can only be achieved by grafting reactions which reduce the lignin content of the polyol to between 40% and 60%. Carboxylation to 10 acid meq/g results in a copolymer with ca. 70% lignin con-tent, and oxyalkylation further reduces this yield in correspondence with the de-sired chain length of the alkylether branches. It is quite obvious that three-di-mensionally branched structure of lignin requires the flexibilizing complementa-tion of a linear chain polymer, yet the extent to which lignin's structural rigidity needs to be softened will also determine the percentage of lignin that can be uti-lized in the manufacture of a commercial polymeric material.

CONCLUSION

It was demonstrated that lignin can serve as the principal raw material for the preparation of a versatile polyol for urethanes by a combination of modification reactions including copolymerization with maleic anhydride and oxyalkylation. The versatility was mainly a result of the types of modification reactions chosen. The foams made from this process were light in color, high in strength, low in water sorption, and had very low density. These products materialized from the particular structural characteristics of the lignin macromolecule, which becomes an integral structural part of the final polyurethane molecule. In the foam, lignin

almost resumes its original function in the tree: to form a three-dimensionally branched bonding network that provides mechanical support to a system of cells and—at the same time—resisting swelling in water.

REFERENCES

[1] H. H. Moorer, W. K. Dougherty, and F. T. Ball, U. S. Patent 3,519,581 (1970).

[2] K. Kratzl, K. Buchtela, J. Gratzl, J. Zauner, and O. Ettingshausen, *Tappi, 45,* 113 (1962).

[3] V. R. Yaunzems, V. N. Sergeeva, L. N. Mozheiko and A. E. Surmonina, Izv. Akad, Nauk Latv. SSR No. 2,232,238; through *Bull. Inst. Paper Chem., 39,* 8543 (1968).

[4] D. T. Christian, S. Leandro, M. Look, A. Nobell, and T. S. Armstrong, U. S. Patent 3,546,199 (1970).

[5] H. Ishikawa, T. Oki and F. Fugita, *Nippon Mokuzai Gakkaishi, 7,* 85 (1961).

[6] G. G. Allen, U. S. Patent 3,476,795 (1969).

[7] K. V. Sarkanen and C. Schuerch, *Anal. Chem., 27,* 1245 (1955).

[8] D. J. David and H. B. Staley, *Analytical Chemistry of the Polyurethanes, Part III,* Wiley-Interscience, New York, 1969,

[9] W. Sandermann, *Svensk Papperstidn., &52,* 365 (1949).

[10] W. Sandermann, C. Schlink, W. Czirnich, and G. Weissman, *Papier, 24,* 187 (1970).

[11] W. G. Glasser, and W. Sandermann, *Svensk Paperstidn., 72,* 246 (1970).

[12] W. G. Glasser and W. Sandermann, *Holzforschung, 24,* 73 (1970).

[13] B. A. Dombrow, *Polyurethanes,* 2nd. ed., Reinhold, New York, 1965.

NAVAL STORES: SILVICHEMICALS FROM PINE

DUANE F. ZINKEL

Forest Products Laboratory,
Forest Service,
United States Department of Agriculture,
Madison, Wisconsin 53705

SYNOPSIS

Of all the silvichemicals that are produced in this country, those from the pines, i.e., naval stores, have the largest aggregate volume and value. Although most naval stores are derived from the pine tree, there are several methods of production, each of which confers specific characteristics upon the common products, rosin and turpentine. The relative importance of these methods has changed, especially over the last decades; byproducts of the kraft pulping process have now become the most prominent source of naval stores. Naval stores have a wide range of uses, from paper sizes to the fine chemicals of flavors and fragrances.

Economics and other factors limit the production of naval stores from traditional sources. Potential new sources are examined, particularly the promising area of induced lightwood formation.

The current Forest Products Laboratory program in naval stores research is reviewed. This includes the development of analytical techniques, chip storage, tall oil neutrals, conversion of sitosterol to pharmaceutical intermediates, lightwood, and resin acid chemistry. In the course of this work, a number of new natural products have been isolated and characterized.

INTRODUCTION

Tree components of spent pulping liquors are the sources of a wide variety of chemical and nonfibrous products known as silvichemicals. This class of materials includes such products as charcoal, naval stores, lignin derivatives, vanillin, essential oils, maple syrup, resins, yeast, alkaloids, tannins, rubber, true gums, ethanol, acetic acid, vitamin pastes, and waxes. Of all the silvichemicals that are produced in this country, those products from pines known as naval stores have the largest aggregate volume and value.

HISTORICAL

A review of the naval stores industry cannot be considered complete unless its lineage is traced to the ancient beginnings, as documented in Genesis (6:14) [1]:

"Make yourself an ark with ribs of cypress; cover it with reeds and coat it inside and outside with pitch." In addition to this application, which continued into the 19th century, naval stores have had many other interesting uses throughout history. For example, naval stores materials found use in lighting (as torches for many centuries and later in turpentine-alcohol lamps); in embalming in ancient Egypt; in weaponry; in pharmaceutical preparations for at least two thousand years; and in drink (nearly 10% of current naval stores production in Greece is used in making the characteristic Greek wine, retsina).

Because of the importance of pitch in keeping a wooden navy afloat, it was essential that any seafaring nation of significance have a controlled and dependable source of supply. The settlement of North America was in large part due to England's desire to rid herself of dependence on Scandinavian sources of naval stores. The American colonial settlers, particularly in Virginia and North Carolina, were charged naval stores products as payment for the charters.

Interesting terminology and jargon developed in this industry during its long history. The still widely used term "colophony," which is derived from the word Colophon (the ancient Greek name for the coastal region and adjacent islands of Western Asia Minor) has been used for centuries to denote either crude pine exudate or rosin. Use of the rather self-descriptive term "naval stores" first appeared in 17th century English records for the naval-related commodities of pitch, tar, and timber. The English sailors became known as Jack Tars because of their intimate contact with the pitch and tar used for calking ships and waterproofing rigging. Because of the large production of naval stores in North Carolina, primarily by the "tar-burning" method, the citizens of that State became known as "tarheels" (tar-burning is the controlled, air-deficient burning of a pile of resinous wood built into the shape of a hive and covered with earth; the tar is collected at the base of the hive). In the 1830s, stills used in the Scotch liquor industry were imported for turpentine production, thus providing the derivation of "spirits of turpentine."

The wound exudate of the pine is commonly termed "pine gum" but it is more correctly referred to as oleoresin. Tree exudates are any material exuded from a tree, usually in response to wounding, and include true gums and oleoresins. (An oleoresin is any natural mixture of essential oil and resin; the respective parts of pine oleoresins are turpentine (the essential oil) and rosin (the resin), both of which are terpenic. True gums are hydrophilic carbohydrates such as gum arabic and gum tragacanth. Pine "gum" is a widespread misnomer for a substance that is not a true gum but, rather, is an oleoresin.) A description and derivation of "tall oil" will be found in a subsequent section of this review.

PRODUCTION OF NAVAL STORES

Naval stores have been produced by a variety of methods. Theophrastus in his "Enquiry into Plants" (ca. 300 BC) chronicled the Macedonian method for making pitch by fire, a method used in this country in the 17th to 19th centuries. Wounding pines and collecting the exudate also has been an important method of naval stores production, particularly during the last 200 years. This "pine gum" exudate was then processed into rosin and turpentine.

During the early to mid-1800s, turpentine was the sought-after product, and the

rosin, being of little value, was usually discarded into waterways. By the 1900s, however, when demands for naval stores products turned to rosin, beds of lakes and streams were mined for the rosin discarded in the previous century.

With the demise of wood ships in commerce, the use of naval stores as such declined, but the industrialization of the nation created new demands. In the early 1900s, a new source for naval stores was exploited. The Yaryan process, originally designed to extract linseed oil from flaxseed with petroleum hydrocarbons, was applied to recovery of naval stores from virgin pine stumpwood from which the sapwood had rotted away. The remaining stump heartwood, which contains about 25% extractives, is chipped, shredded, extracted, and the extract processed further. The destructive distillation of resinous wood (including stump heartwood) in retorts was a significant factor, at one time, in the production of comparatively low-quality naval stores products. Only one small plant remains in production in the United States, however.

More recently, byproducts have been recovered from the kraft pulping of pine. It wasn't until the 1930s that the byproduct "tall oil" was first introduced as a commodity in this country. It made little impact on the American naval stores market until World War II, when substitutes were needed for inedible fats and oils.

CURRENT SOURCES

Today's naval stores are of three types: ·gum, wood, and sulfate, which contribute 4%, 39%, and 57%, respectively, to current United States production (combined rosin and turpentine).

Gum naval stores. These are produced by wounding pines and collecting the oleoresin, which is processed into rosin and turpentine. In this country, the gum naval stores industry is based on two southern pine species, slash (*Pinus elliottii*) and longleaf (*P. palustris*), and is now centered in the State of Georgia.

Wood naval stores. (Also known as steam-distilled naval stores, though steam is no longer used in the processing.) These consist of a turpentine, a pine oil frac-

FIG. 1. Recovery of naval stores by-products from kraft pulping process.

ZINKEL
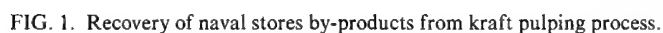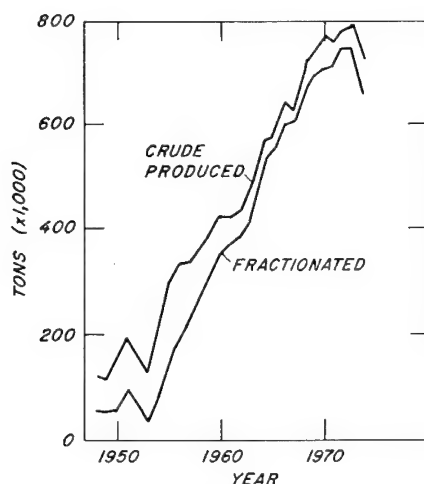
FIG. 2. Tall oil production and fractionation in the United States.
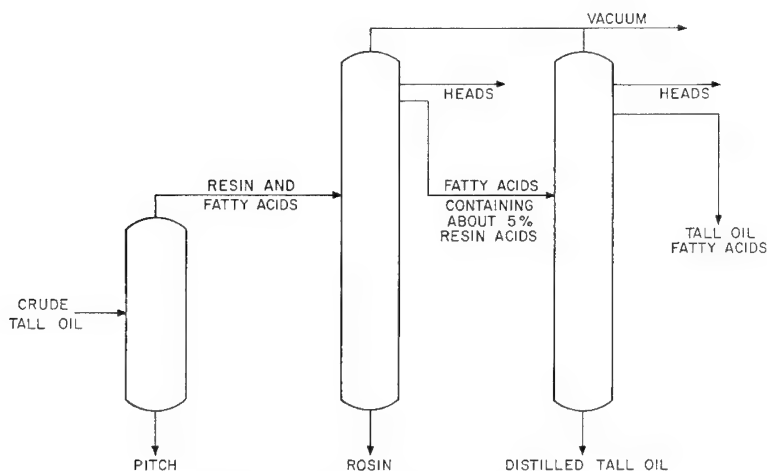
FIG. 3. Fractionation of crude tall oil.

tion, and a crude resin. This dark-red resin is further purified by selective absorp-
tion on fuller's earth or by extraction with furfural. A decolorized wood rosin and
a dark pitch-like product are obtained.

Sulfate naval stores. These are derived as byproduct streams from the kraft
pulping process (Fig. 1). As pine chips are cooked to produce pulp, the volatilized
gases are condensed to yield sulfate turpentine. On cooking the chips, the alkaline
pulping liquor also saponifies the fats and converts the fatty and resin acids to the
sodium salts. In recovering the pulping chemicals, the aptly named black liquor is
first concentrated in multiple-effect evaporators. The concentrate moves to a set-
tling tank where the soaps rise to the surface to be removed by a mechanical skim-
mer. This soap skimming is acidified to yield crude tall oil.

The term "tall oil" is derived from the Swedish word "tallolja," which translates
as pine oil. However, such literal translation would have caused confusion with
the essential oil known as pine oil. Thus, the simple transliteration to tall oil.

Crude southern tall oil contains 40%–60% resin acids, 40%–55% fatty acids and 5%–10% neutral constituents. During the early years of the recovery process, most tall oil was burned for fuel. Although distillation units for tall oil purification provided commercial products from the mid-1930s, commercial-scale production of high-purity fatty acids and rosin was not demonstrated until 1949. After 1955, the rate of tall oil production and fractionation increased rapidly (Fig. 2).

By far the major portion of tall oil is now being fractionated (Fig. 3) into tall oil rosin and fatty acids. One ton of tall oil yields approximately 600 lb of fatty acids, 700 lb of rosin, and 700 lb of intermediate, head, and pitch fractions. The United States's fractionating capacity is about 1 million tons per year, over twice that of the rest of the world.

Tall Oil Fatty Acids

Tall oil fatty acid products are available with resin acid contents from about 15%–40% (distilled tall oil) down to less than 0.5%. These fatty acids consist primarily of n-C_{18} acids, of which 75% are the monoenoic (oleic) and the dienoic (linoleic) acids with but small amounts of the trienoic and saturated acids. The linoleic fraction is mostly the cis-9,12 compound with some isomerization products. A 5,9-linoleic acid has been found in small amounts in tall oil and pine extractives. Several other unsaturated fatty acids—the 5,9-C_{18} dienoic; 5,9,12-C_{18} trienoic;
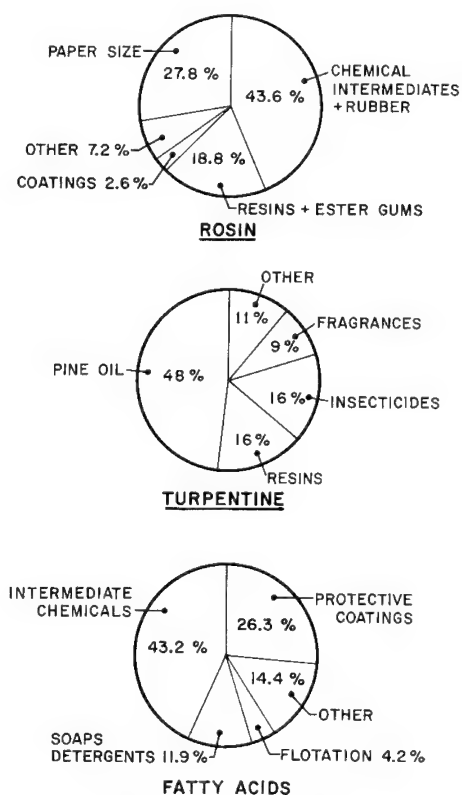
FIG. 4. Naval stores uses.

linolenic; the cis-11-C_{20} monoenoic; and the 5,11,14-C_{20} trienoic acids—have been found in small amounts in various tall oils and pine extractives.

Other specialty tall oil fatty acid products are also available. One such product, obtained from tall oil heads, contains predominately saturated fatty acids, of which 55% is palmitic. Others are a commercial oleic acid (the monoenoic portion is composed of about equal amounts of oleic acid and its trans isomer, elaidic acid, the latter being formed by isomerization during removal of the linoleic acid) and various commercial linoleic acid products.

Of the over 1 billion lb of fatty acids produced in this country, about 35% comes from tall oil. Major uses for tall oil fatty acids (Fig. 4) are in protective coatings, intermediate chemicals (a catchall category, of which the major uses are for epoxy tallates, and for dimer acids that, in turn, are used in polyamide resins for inks, adhesives, and coatings), soaps and detergents, and as flotation agents. A further discussion of tall oil fatty acids and of tall oil rosins can be found in [2].

Rosin

Rosins from the xylem portion of pine trees consist primarily of diterpene resin acids of the abietic type (abietic, neoabietic, palustric, levopimaric, and dehydroabietic) and pimaric type (pimaric, isopimaric, and sandaracopimaric), as shown in Figure 5. Although the abietic-type levopimaric acid is present in substantial amounts in southern pine, it is readily isomerized to the other abietadienoic acids and does not survive normal processing.

Small amounts of neutral materials such as anhydrides, phenolics, sterols (mainly sitosterol), diterpene aldehydes, and alcohols are also present in rosins.
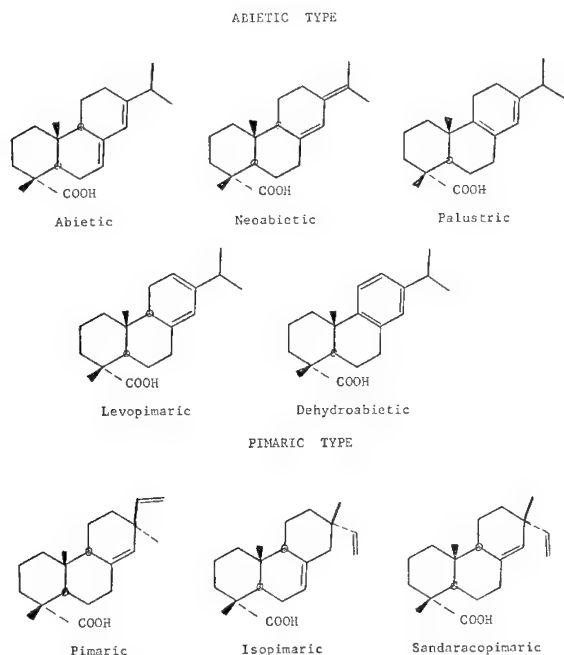
FIG. 5. Common resin acids of pine.
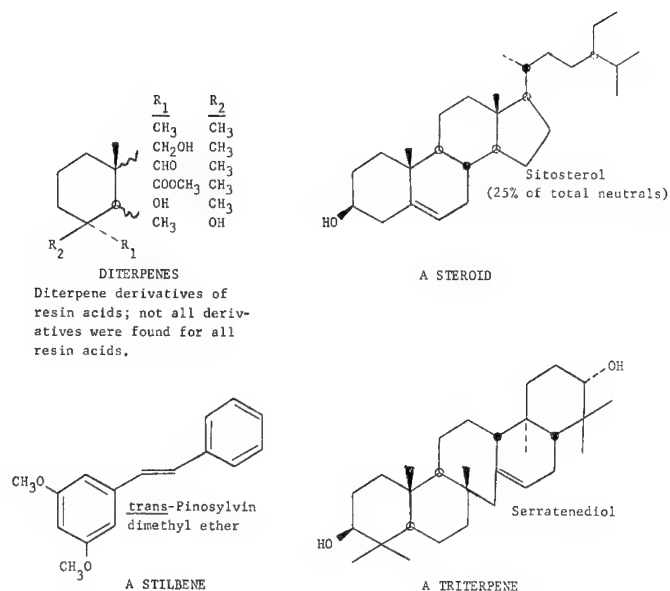
FIG. 6. Examples of neutral materials in tall oil soaps.
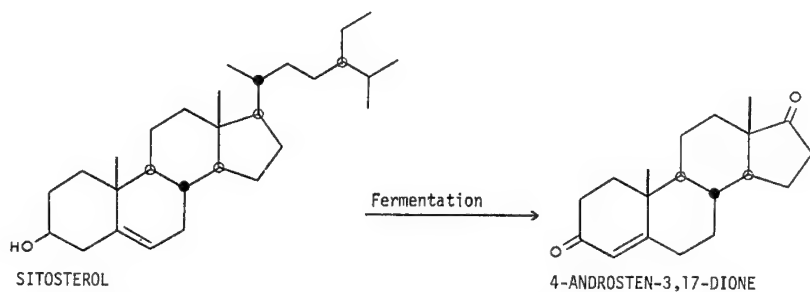
. FIG. 7. Example of the fermentation of sitosterol to various androstane, progestane, and estrane derivatives.

Some examples of these neutral materials are shown in Figure 6. Conner and Rowe [3], of the Forest Products Laboratory, have recently conducted a quantitative analysis of the neutrals of crude tall oil soaps in which they have identified 80 compounds, including all those present at the 0.1% level or better. The neutral materials have no commercial value of their own and often detract from the value of the rosin. However, the relatively pure sitosterol could have potential as a precursor in the synthesis of steroids (Fig. 7).

The difference in properties and uses (Fig. 4) of commercial rosins depends both on the kind and quantity of the neutral components and on the relative composition of the resin acids. Typical resin acid composition data are given in Table I. High proportions of the conjugated abietadienoic acids are best for preparing the maleic modified (i.e., the maleic anhydride Diels-Alder) product. High proportions of individual resin acids result in increased tendency to crystallize, thus causing problems in handling. For many purposes, rosins and rosin derivatives are interchangeable regardless of source.

TABLE I
Typical Distribution of Principal Resin Acids in Rosins

Type	Abietic	Neo-abietic	Palustric	Dehydro-abietic	Pimaric	Isopimaric
	%	%	%	%	%	%
Gum	22	20	25	6	5	17
Wood	50	5	10	13	6	13
Tall oil	32	4	10	30	4	10

Rosins are used mostly in some modified form: Hydrogenated, dehydrogenated, disproportionated, esterified, polymerized, as salts, or reacted with formaldehyde or maleic anhydride, for example. The largest use is in the sizing of paper to control water absorptivity. A rosin soap or emulsion is added to the pulp and is precipitated onto the paper fibers with aluminum sulfate.

Although rosin found considerable use at one time in the old yellow bar laundry soaps (38% of rosin was used for this purpose in 1938), this use is almost negligible now. Rosin soaps, however, find important use as emulsifying and tackifying agents in synthetic rubber manufacture. Other uses for rosin are in adhesives, surface coatings, printing inks, and chewing gum.

The United States contributes about 37% of current world rosin production, followed by the USSR, Mainland China, Portugal, and Mexico.

Turpentine

The major market for turpentine once was as a solvent in paints, but in the past 10 years, it has been increasingly used as a chemical raw material. Coupled with this change was an increase in the price of gum turpentine from 20 cents per gal. in 1962 to $1.60 in 1975. As the fractionated components have specific uses, the composition of the turpentine is important; typical compositions are shown in Figure 8. Of the turpentine types, sulfate turpentines can have the greatest varia-

	Gum	Wood	Sulfate
α-Pinene	60-65%	75-80%	60-70%
β-Pinene	25-35	0-2	20-25
Camphene	--	4-8	--
Other Terpenes	5-8	15-20	6-12

α-Pinene   β-Pinene   Camphene Δ^3-Carene
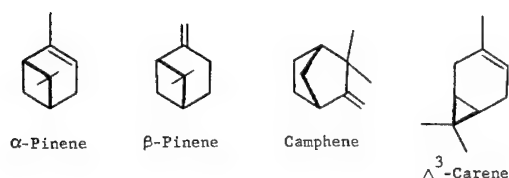
FIG. 8. Composition of turpentines.

tions because of the number of species pulped and the large geographical range from which they are taken. Western sulfate turpentine has appreciable amounts of Δ^3-carene (as do Asian and European turpentines), but this component has only limited uses other than as a solvent. The United States currently produces about 38% of the world's turpentine, followed by the USSR, Mainland China, and Portugal.

The major use of turpentine (Fig. 4) involves the conversion of α-pinene with aqueous mineral acids to synthetic pine oil whose primary constituent is α-terpineol. The process can be controlled to favor further hydration to form the well-known expectorant, terpin hydrate.

α-Pinene   α-Terpineol   Terpin hydrate
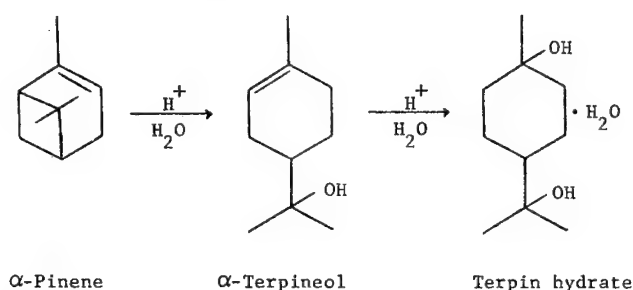
Variations in the synthetic conditions, fractionation, and blending give pine oils with different properties. These pine oils find use in mineral flotation, in processing textiles, as solvents, as odorants, and as bactericides. Over 80% of the pine oil produced is synthetic; the remainder is the so-called natural pine oil that is obtained on fractionation of the stumpwood extractives.

The second largest and growing use of turpentine is in the production of polyterpene resins. A large variety of low molecular-weight (600–1500 mol wt) polymers are produced from β-pinene, mixtures of α- and β-pinene, and pyrolyzed α-pinene (i.e., a mixture consisting primarily of dipentene and alloocimene). The largest use for these terpene resins is in adhesives, particularly in the compounding of pressure-sensitive adhesives such as transparent tapes. Other uses are in chewing gum, drycleaning sizes, and in paper sizes.

The terpene insecticides are based on camphene, which is obtained either from wood turpentine or by isomerization of α-pinene. The toxaphene-type insecticides are prepared by chlorinating camphene or camphene-α-pinene mixtures, to form products having an approximate empirical formula of $C_{10}H_{10}Cl_8$. The future of these chlorinated insecticides, however, is uncertain.

Perhaps the most interesting area of turpentine utilization is in the small but growing production of flavor and fragrance chemicals. Synthesized products such as lemon, lime, peppermint, spearmint, and nutmeg essential oils are being marketed along with a wide range of fine chemicals for the flavor and fragrance industry. Examples of the synthetic routes to these fine chemicals are shown in Figure 9.

One major route involves the pyrolysis of β-pinene to form myrcene. The addition product of myrcene and HCl is reacted with sodium acetate to form the acetates of linalool, geraniol, and nerol, which can then be hydrolyzed to the corresponding alcohols. The reaction conditions can be controlled to yield either linalool or geraniol-nerol products. Linalool and its esters have lilac-like fragrances. Geraniol and nerol and their esters are rose-like as is their hydrogenation product,
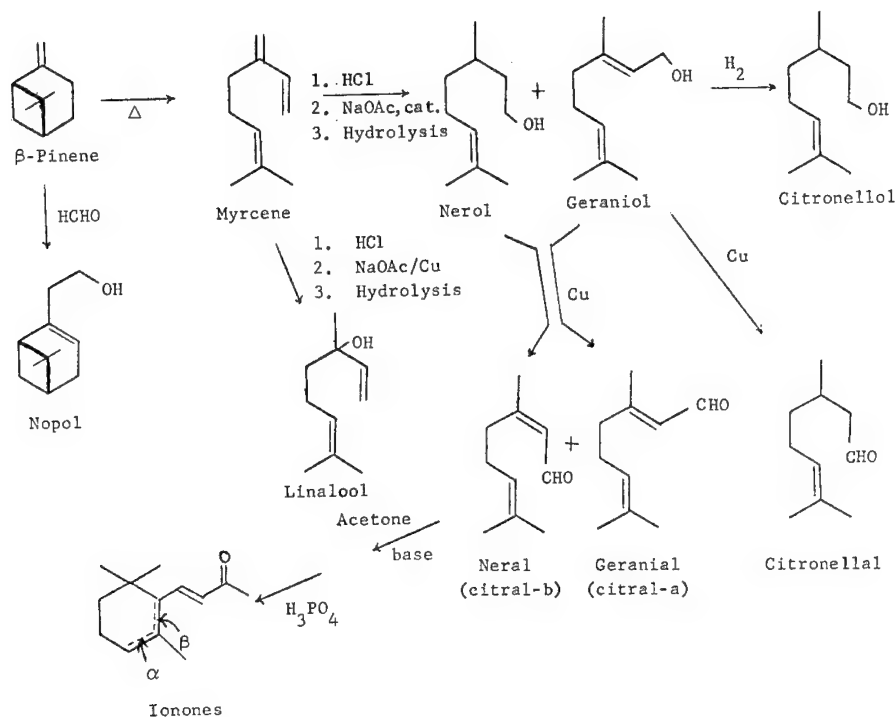
FIG. 9. Synthesis of some fragrance and flavor chemicals from β-pinene.

citronellol.   Rearrangement of geraniol-nerol over copper catalyst produces either citronellal or a mixture of citrals (geranial and neral), depending on the conditions used.   Citronellal finds use as an odorant and can be reduced to citronellol or hydrated (via the bisulfite adduct to prevent cyclization) to hydroxycitronellal, which has a lily-of-the-valley fragrance.   Citral is used for its intense lemon character in the preparation of citrus flavors and fragrances.   Condensation of citral with acetone followed by isomerization produces a mixture of the violet fragrance ionones. The beta isomer is used as an intermediate in the synthesis of vitamin A.

The reaction of β-pinene with formaldehyde yields nopol, a "nonnatural" product that is used in perfumery.   The acid-catalyzed addition of acetic acid to α-pinene produces isobornyl acetate, a product having a characteristic pine-needle scent.
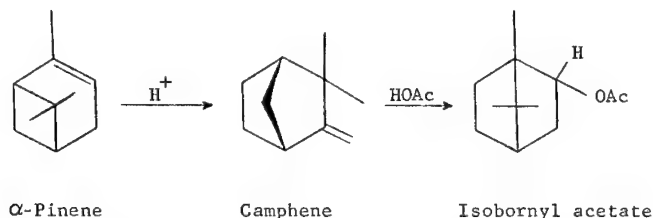
The synthesis of menthol is shown in Figure 10:   The ℓ-isomer is obtained from ℓ-β-pinene through a sequence of reactions to d-citronellal to ℓ-isopulegol to product.   Racemic menthol is obtained as a byproduct of this process and also by a series of steps, beginning with the oxidation of 3-menthene.   Menthol is used for its cooling effect in cigarettes and cosmetics (the ℓ-isomer is most active) and in flavoring, particularly peppermint.
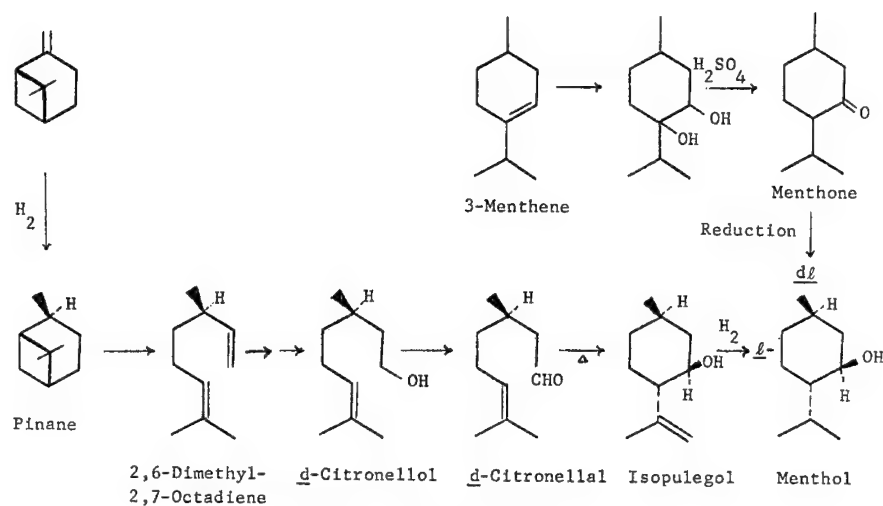
FIG. 10. Synthesis of menthol.

A number of other monoterpene products are obtained by esterification, fractionation of turpentine or the reaction products described above, and by other processes. In addition to terpenes, turpentine is a source of phenolic-type flavor and fragrance materials. Estragole (methyl chavicol) and anethole are both isolated during fractionation. The estragole can be isomerized to anethole, which is well-known for its licorice-anise flavor. Oxidation of anethole produces anisaldehyde, which has wide use in perfumery because of its hawthorne or coumarin-type fragrance.

Methyl chavicol   Anethole   Anisaldehyde
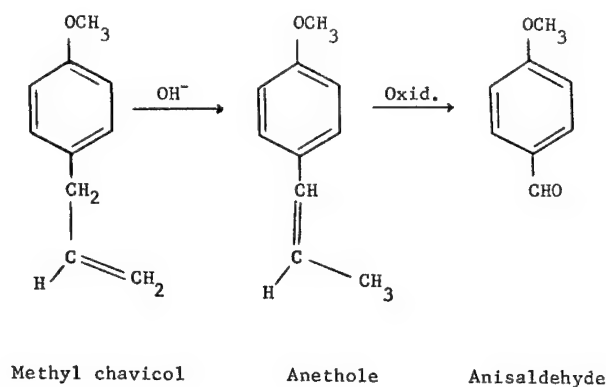
OUTLOOK FOR PINE SILVICHEMICALS

Current Technology

By some standards, naval stores is not a large industry. Nevertheless, yearly product volume is near 1 billion lb with a value of about $300 million. Although pine chemicals have faced competition from other agricultural commodities and petrochemicals, the most serious problem is lack of supply. Past and present
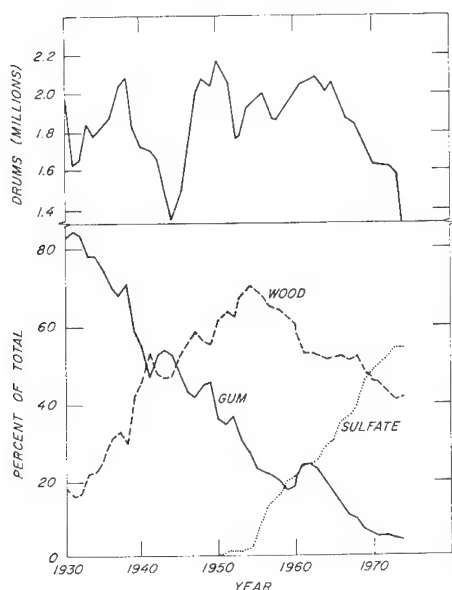
FIG. 11. Production of rosin in the United States: Top, in drums (520 lb); bottom, by source.
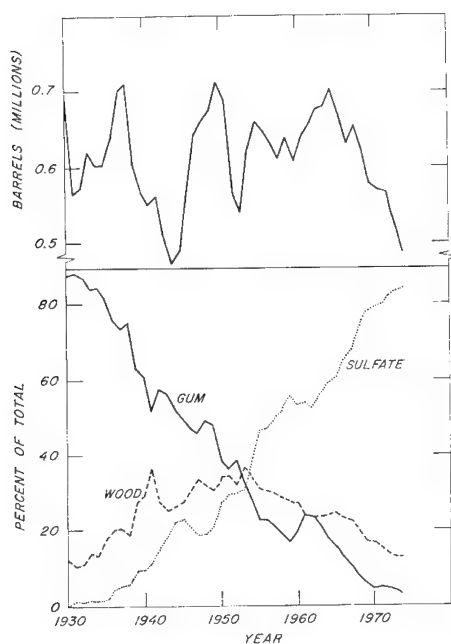
FIG. 12. Production of turpentine in the United States: Top, in barrels (50 gal); bottom, by source.

United States output of rosin and turpentine from the three sources are compared in Figures 11 and 12.   Whereas only 4% of United States naval stores are of the gum type, overall world production from this source is about 50%.

In this country, escalating labor costs and shortage of raw material have caused major decreases in rosin and turpentine production from virgin pine stumps.   Second growth stumps are not satisfactory because there is not sufficient heartwood

for economical processing.   Although there is a large supply of ponderosa pine stumps [4], the extract has a high content of neutrals which affects either the product quality or cost of processing.   Escalating labor costs, and the social stigma of the work have severely decreased naval stores production from gum (oleoresin) farming.

Recovery of kraft pulping byproducts has increased dramatically but has not been able to compensate completely for the loss in production from the other sources.   Output of these byproducts is correlated, obviously, with production of kraft pulp from pine and is further influenced by wood sources, wood storage, pulping, recovery efficiency, and byproduct processing.   No drastic changes in output of pine chemicals from pulping byproducts appear likely in the immediate years ahead.   Unless the economics change to stimulate greater production from oleoresin and pine stumps, new sources of pine silvichemicals will be needed.

Potential Sources

One of the most promising developments is the result of research at the U.S. Forest Service Naval Stores and Timber Production Laboratory (Olustee, Fla.). Scientists there discovered that treatments of pines with certain dipyridyl herbicides stimulate extensive oleoresin formation and diffusion into the wood substance [5].   Some samples of the wood have extractive contents of 40% (green weight basis) [6].   Such oleoresin-soaked wood is known as lightwood, despite its relatively high density, because it burns easily.

In the tree the zone of lightwood formation extends to the pith (Fig. 13), and many feet above the treatment level.   It should be noted that the increase in ex-
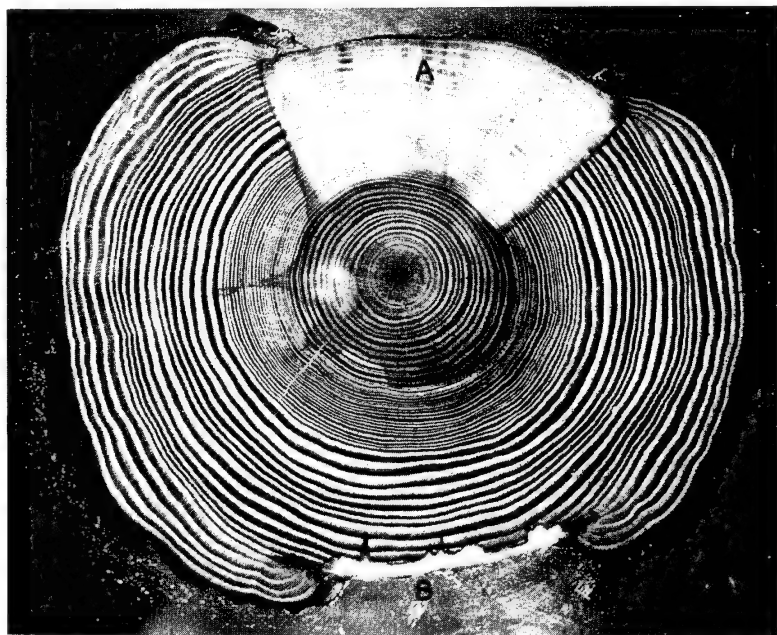
FIG. 13. Induced lightwood formation on treatment of longleaf pine: (A) with the herbicide paraquat; (B) compared with limited resin-soaking during normal gum tapping.

tractives is due solely to oleoresin, i.e., rosin and turpentine. The effectiveness of the treatment with different pines, the response from other conifers, treatment levels, schedules, and many other variables are currently under investigation. Application of the herbicides appears to be a simple, low-cost operation that will either increase yields of sulfate naval stores or provide a new type of wood naval stores by extraction of the resin-saturated wood prior to pulping (or a combination of both methods).

Should the induced lightwood technology be successfully developed, the initial effect would be to stabilize production against chronic shortages and thus secure current markets. This would be beneficial to the entire naval stores industry. With further implementation of the technology, sufficient supplies of naval stores would be available for new, large-volume markets. Although turpentine could well recover a major share of its old market as a solvent for oil-based alkyd paints, the size of this market is limited because of greatly diminished use of these alkyds in the past few years. Continued market growth for chemical products from turpentine can be expected. Some consideration is being given to the incorporation of turpentine into automobile fuel formulations.

The future utilization of rosin with respect to new, large-volume markets will be based on chemical composition and reactivity. This not only relates to the type (source) of rosin but also to the pine species from which it originates. For example, longleaf or loblolly pine rosins have a much higher content of the reactive abietadienoic acids than does slash pine rosin. However, loblolly pine, the most important southern pine pulpwood species, is a very poor gum oleoresin producer. Thus, application of this new technology will allow a greater flexibility in the
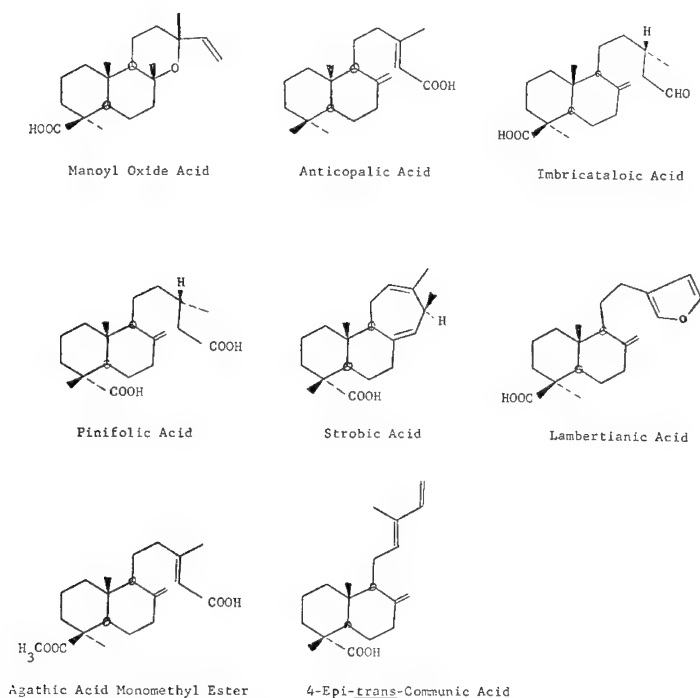
FIG. 14. Unusual resin acids in pine needles.

species involved in naval stores production with a possible new dimension in the tailoring of rosins.

Another potential source, although not as promising, is the foliage portion of logging residues [7]. A limited quantity of a high quality pine oil is presently distilled from some southern European species; Scots pine has also been considered a source of oil [8]. Much has been published in the Russian literature [9] on products from conifer needles; vitamin (A and E) preparations are being produced in several plants in the Soviet Bloc [30]. Although little is known about the terpene components of pine needles, we have found that the needles of a number of pines contain resin acids which are quite different from the common array found in wood. In certain pine species, a single diterpene resin acid (several of which are shown in Fig. 14) predominates in the needle resin and can be readily purified; these resin acids have potential for fine chemical uses. The extracted needle residue has possible use as a roughage type of cattlefeed.

RESEARCH

At one time, the use of naval stores products was only on the basis of their gross physical or physical-chemical properties. Now, however, utilization is more and more being based on chemical properties. In many instances, this involves preseparation of constituents and processing into high-quality fine chemicals; the utilization of turpentine is a notable example. This progress is the result of increasing research at all levels. In addition to the product development research being conducted in the laboratories of a number of pine chemicals companies, and the "basic" research at many universities, important contributions have come from government laboratories. For many years, the Naval Stores Laboratory at Olustee, Fla., made major contributions in the chemistry and processing of turpentine and rosin, particularly with regard to gum (oleoresin) naval stores. (Note: The Naval Stores Laboratory, Agricultural Research Service, U.S.D.A., which closed June 30, 1973, is distinct from the previously mentioned Naval Stores and Timber Production Laboratory of the U.S. Forest Service.)
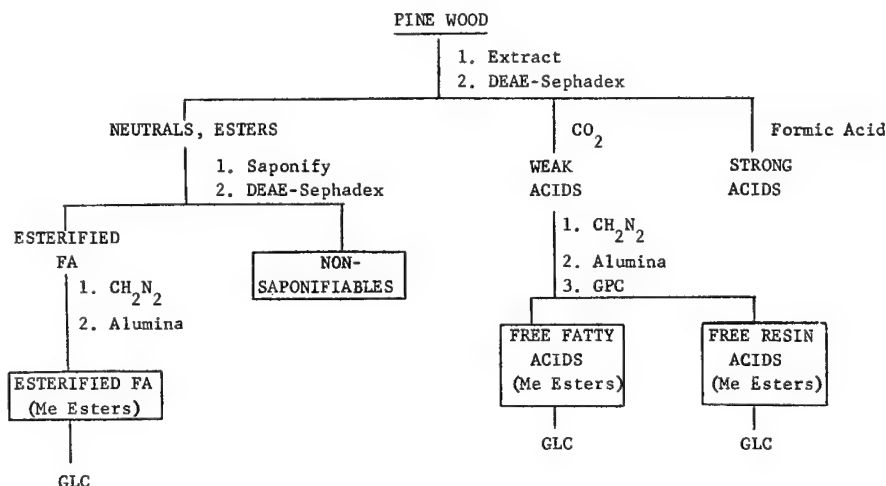
FIG. 15. Analytical scheme for pine extractives.

TABLE II
Resin Acids of Pines and Naval Stores

Common Name	Systematic Name[a]	Year of Discovery	Occurrence[b]
Abietic (Fig. 5)	7,13-abietadien-18-oic	1910	Widespread
Levopimaric (Fig. 5)	8(14),12-abietadien-18-oic	1887	Oleoresins and extractives
Neoabietic (Fig. 5)	8(14),13(15)-abietadien-18-oic	1948	Widespread
Palustric (Fig. 5)	8,13-abietadien-18-oic	1960[11]	Widespread
Dehydroabietic (Fig. 5)	8,11,13-abietatrien-18-oic	1938	Widespread
Dehydrodehydroabietic	6,8,11,13-abietatetraen-18-oic	1969	Rosin[12]
------	7,13,15-abietatrien-18-oic	1975	Extraction artifact[13]
Secodehydroabietic	2α-[2'-(m-isopropylphenyl)ethyl]-1β,3α-dimethylcyclohexanecarboxylic	1969	Tall oil fraction[14]
A tetrahydroabietic	?(published data not consistent with pure tetrahydroabietic acids)	1966	P. ponderosa heartwood[15] (artifact?)
Pimaric (Fig. 5)	8(14),15-pimaradien-18-oic	1887	Widespread
Δ^8-Pimaric	8,15-pimaradien-18-oic	1969	Tall oil fraction[14]
Isopimaric (Fig. 5)	7,15-isopimaradien-18-oic	1948	Widespread
Sandaracopimaric (Fig. 5)	8(14),15-isopimaradien-18-oic	1966	P. elliottii oleoresin,[16] widespread
Δ^8-Isopimaric	8,15-isopimaradien-18-oic	1966	P. elliottii oleoresin,[16] widespread
Strobic (Fig. 14)	$14\underline{\xi}$,17-cyclolabda-8(17),12-dien-18-oic	1973	P. strobus cortex,[17] P. quadrifolia[18]

Imbricataloic (Fig. 14)	15-oxo-8(17)-labden-19-oic	1971	P. elliottii[19] and P. ponderosa[12] needles, needles of a number of sp.
Imbricatoloic	15-hydroxy-8(17)-labden-19-oic	1971	P. elliottii[19]
Lambertianic (Fig. 14)	15,16-epoxy-8(17),13(16),14-labdatrien-19-oic	1966	P. lambertiana wood,[20] needles of several species[12]
Pinifolic (Fig. 14)	8(17)-labdene-15,18-dioic	1962	P. silvestris needles[21]
Dehydropinifolic	8(17),E-13-labdadien-18-oic	1971	P. silvestris needles[22]
Agathic acid monomethyl ester (Fig. 14)	Methyl 8(17),E-13-labdadien-15-oic-19-oate (acid)	1974	P. massoniana needles[23]
Mercusic (dihydroagathic)	8(17)-labdene-15,19-dioic	1974	P. merkusii oleoresin[24]
Manoyl oxide (acid) (Fig. 14)	8,13β-epoxy-14-labden-19-oic	1971	P. resinosa, P. nigra needles[12]
Epimanoyl oxide (acid)	8,13-epoxy-14-labden-19-oic	1972	P. resinosa needles[12].
trans-Communic (elliotinoic)	8(17),E-12,14-labdatrien-19-oic	1965	P. elliottii oleoresin,[25] some other sp.
Epicommunic (Fig. 14)	8(17),E-12,14-labdatrien-18-oic	1975	P. densiflora,[12] some traces of P. nigra (needles)[12]
Anticopalic (Fig. 14)	8(17),E-13-labdadien-15-oic	1971	P. monticola wood,[26] P. strobus needles[27]
3-Ketoanticopalic	3-oxo-8(17),E-13-labdadien-15-oic	1975	P. strobus needles[12]
3β-Acetylanticopalic	3β-acetoxy-8(17),E-13-labdadien-15-oic	1974	P. bungeana, P. strobus needles[12]
8-Hydroxyanticopalic	8-hydroxy-E-13-labden-15-oic	1975	P. strobus cortex[12]

aThe systematic nomenclature follow the proposals of a committee chaired by J. W. Rowe [29].

bOnly the most recently discovered resin acids are referenced.

Research on the common precursors of all naval stores, i.e., the extractives in pine, is being conducted at the Forest Products Laboratory in Madison, Wis., in cooperation with the Pulp Chemicals Association. An analytical procedure (Fig. 15) has been devised [10] which integrates several unique approaches in chromatographic techniques to give a detailed and quantitative picture of the constituents of pine extractives. The DEAE-Sephadex step avoids the problems inherent in the classical separation of neutrals from acids via extraction of a soap solution; the gel-permeation step avoids problems in interpretation of the gas chromatographic data that occur if the fatty and resin acids are analyzed in admixture. This analytical scheme has provided valuable data on pine extractives of various tissues, on changes in constituents during chip storage and pulping, and has been invaluable in the detection and isolation of new natural products, in particular, diterpene resin acids.

The current status as to the resin acids known in pine and naval stores is summarized in Table II. A large number of the new resin acids have been found in pine needles. Although these are not of commercial importance at present, they are of practical application in genetics such as in provenance studies and in investigations of intra- and interspecific hybridization. In the course of naval stores research at the Forest Products Laboratory, high purity diterpene resin acid methyl esters were used in obtaining a series of high-quality standard spectra, many of which have been published as a compilation [29] with supplements to be issued periodically.

SUMMARY

Insufficient supply remains the long-term problem with naval stores commodities, even though crude tall oil and its products were temporarily plentiful when this paper was written. The naval stores industry is in the midst of transition from the traditional pattern, both in source of raw material supply and in processing to more sophisticated chemical products.

Production of naval stores goes hand in hand with multiple uses and products of the forest, one of the Nation's most valuable and renewable natural resources. Although many doomsday prophecies have been made about the naval stores industry, it remains viable. Because of the renewability of its resource, this pine silvichemical industry promises to endure far into the future.

REFERENCES

[1] *The New English Bible,* (1970).
[2] B. F. Ward, Jr., *Appl. Polym. Symp.* No. 28, (Pt. 1) 329 (1975).
[3] A. H. Conner, and J. W. Rowe, *J. Amer. Oil Chem. Soc., 52,* 334 (1975).
[4] N. M. Joye, Jr., A. T. Proveaux, R. V. Lawrence, and R. L. Barger, *Ind. Eng. Chem., Prod. Res. Develop., 8,* 297 (1969).

[5] D. R. Roberts, "Inducing Lightwood in Pine Trees by Paraquat Treatment," USDA Forest Service Research Note SE-191, Southeastern Forest Experiment Station, Asheville, N.C., April 1973.

[6] D. R. Roberts, N. M. Joye, Jr., A. T. Proveaux, W. J. Peters, and R. V. Lawrence, *Naval Stores Rev., 83,* 4 (1973).

[7] J. L. Keays, "Complete-Tree Utilization, An Analysis of the Literature, Part II: Foliage," Information Report VP-X-70, Canadian Forestry Service, Vancouver, B.C. (1971).

[8] K. Hannus, and G. Pensar, *Pap. Puu, 55,* 509 (1973).

[9] R. I. Tomchuk, and G. N. Tomchuk, "Tree Foliage and Its Utilization in the National Economy," Moscow (1973).

[10] D. F. Zinkel, *Tappi, 58(1),* 109 (1975).

[11] W. H. Schuller, R. N. Moore, and R. V. Lawrence, *J. Amer. Chem. Soc., 82,* 1734 (1960).

[12] D. F. Zinkel, unpublished.

[13] D. F. Zinkel, *Tappi, 58(2),* 118 (1975).

[14] D. F. Zinkel, J. W. Rowe, L. C. Zank, D. W. Gaddie, and E. R. Ruckel, *J. Amer. Oil Chem. Soc., 46,* 633 (1969).

[15] R. Riffer, and A. B. Anderson, *Holzforschung, 20,* 36 (1966).

[16] N. M. Joye, Jr., R. V. Lawrence, and L. J. Gough, *J. Org. Chem., 31,* 320 (1966).

[17] D. F. Zinkel, and B. P. Spalding, *Tetrahedron, 29,* 1441 (1973).

[18] D. F. Zinkel, and A. H. Conner, *Phytochem., 12,* 938 (1973).

[19] B. P. Spalding, D. F. Zinkel, and D. R. Roberts, *Phytochem., 10,* 3289 (1971).

[20] W. G. Dauben, and V. F. German, *Tetrahedron, 22,* 679 (1966).

[21] C. Enzell, and O. Theander, *Acta Chem. Scand., 16,* 607 (1962).

[22] T. Norin, S. Sundin, and O. Theander, *Acta Chem. Scand., 25,* 607 (1971).

[23] D. F. Zinkel, and W. B. Critchfield, *Phytochem., 13,* 2876 (1974).

[24] G. Weissmann, *Holzforschung, 28,* 186 (1974).

[25] N. M. Joye, Jr., E. M. Roberts, R. V. Lawrence, L. J. Gough, M. D. Soffer, and O. Korman, *J. Org. Chem., 30,* 429 (1965).

[26] D. F. Zinkel, J. K. Toda, and J. W. Rowe, *Phytochem., 10,* 1161 (1971).

[27] D. F. Zinkel, and B. P. Spalding, *Phytochem., 11,* 425 (1972).

[28] J. W. Rowe, "The Common and Systematic Nomenclature of Cyclic Diterpenes," USDA, Forest Service, Forest Products Laboratory, Madison, Wis., (1968, with Addenda and Corrigenda, 1969).

[29] D. F. Zinkel, L. C. Zank, and M. F. Wesolowski, "Diterpene Resin Acids. A Compilation of Infrared, Mass, Nuclear Magnetic Resonance, Ultraviolet Spectra and Gas Chromatographic Retention Data," USDA, Forest Service, Forest Products Laboratory, Madison, Wis., (1971).

[30] T. L. Keays, "The Practical Utilization of Foliage," *Appl. Polym. Symp.,* No. 28 (Pt. 2), in press.

General Interest Sources

Kirk-Othmer Encyclopedia of Chemical Technology (See "Terpenes and Terpenoids," "Rosin and Rosin Derivatives," "Tall Oil," and "Turpentine.") 2nd Ed., John Wiley & Sons, New York (1968-9).

"Demand and Price Situation for Forest Products 1972-3," USDA Misc. Publication No. 1239 (1973).

"Naval Stores, History, Production, Distribution and Consumption," T. Gamble, ed., Review Publishing Co., Savannah (1921).

"Naval Stores Review International Yearbook 1972-73," Naval Stores Review, New Orleans (1974).

TALL OIL—CHEMICALS FROM A NATURAL, RENEWABLE SOURCE

BENJAMIN F. WARD, JR.

Chemical Division,
Westvaco Corporation,
Charleston Heights,
South Carolina 29405

SYNOPSIS

During the past 20 years the tall oil industry has matured. The challenge is no longer how to get rid of this by-product at a profit, but how to optimize production and obtain all of the raw material possible. This work traces the history of the industry and discusses some of the future changes that can be expected. Techniques for increasing yields and improving the recovery of tall oil are being actively pursued throughout the industry. Complete utilization of the crude oil has become extremely important, so the component parts of tall oil have now been isolated and are being utilized in the production of a variety of specialty chemicals. The production and utilization of these chemicals will be reviewed with emphasis on the variety of end uses open to the industry. The long-range potential for this renewable chemical will be discussed as we try to outline the future challenge for this widely used tree-derived chemical mixture—tall oil.

INTRODUCTION

The rapidly growing pine trees so prominent in the southeastern portion of the United States provide an excellent, easily renewable source of lumber, pulp, and chemicals. Traditionally the lumber and pulp have been considered to be the major products of these trees, and the chemicals generally were considered to be a disposal problem. During the last few decades, however, the recovery and utilization of these chemicals has become extremely important. The major industry based on waste of the kraft pulping process is the tall oil industry. Tall oil is basically a mixture of rosin acids, fatty acids and alcohols which is separated from the fibers during the chip-cooking process. The pine tree contains about 2% tall oil as it stands, but by the time it is shipped to the mill and processed, only about half of the tall oil originally present is recovered. As the kraft paper industry has grown, so the tall oil industry has grown: from 190,000 tons of crude tall oil produced in

1948 to about 900,000 tons in 1973. Less than 30% of the crude tall oil was refined in 1948, whereas in recent years about 90% has been refined.

There are eight domestic refiners of crude tall oil with 14 refineries. There are also small refineries in Canada and Europe, and a large refinery in Japan. Worldwide, the refinery capacity exceeds the crude tall oil available and the production of crude tall oil seems to be level now rather than growing. Nevertheless, the demand for refined tall oil promises to remain very strong, since the tall oil industry provides basic renewable chemicals to numerous industries and is broadening continuously the utility of its products. In 1974 sales of tall oil-based chemicals exceeded one-quarter of a billion dollars. Whether or not this production will increase in the future depends on the development of improved recovery of chemicals in the pulp mills and the successful utilization of chemicals to improve the tree's production of tall oil.

Before discussing the utilization of tall oil products, it would be helpful to review the general processing involved in the production of the basic product line. First of all, as the cooking liquor from the pulping process is concentrated, the sodium salts of the tall oil acids, being less dense, float to the top and are skimmed off. Soap skimmings recovery seems to be optimized between 25%–30% black liquor solids. Soap skimmings are acidified with sulfuric acid to release the crude tall oil and leave a sodium sulfate brine which is utilized by the pulp mill. The crude tall oil normally is refined in a series of distillations. The exact design varies from refinery to refinery, but all follow the basic scheme shown in Figure 1, using a multicolumn distillation. The yields of each product vary from one refinery to the other, depending on equipment, design, and quality of the crude tall oil; however, the approximations given in Figure 1 are representative of the industry. The designing of columns to separate fatty acids and rosin acids efficiently has been a real challenge for the industry due to the inherent oxygen instability at elevated temperatures and the multitude of impurities which have a broad range of boiling points. Both primary fractions are very high boiling; therefore, low vapor

CRUDE TALL OIL

TALL OIL HEADS   10%

TALL OIL FATTY ACIDS   35%

DISTILLED TALL OIL   5%

TALL OIL ROSIN   30%

PITCH   20%
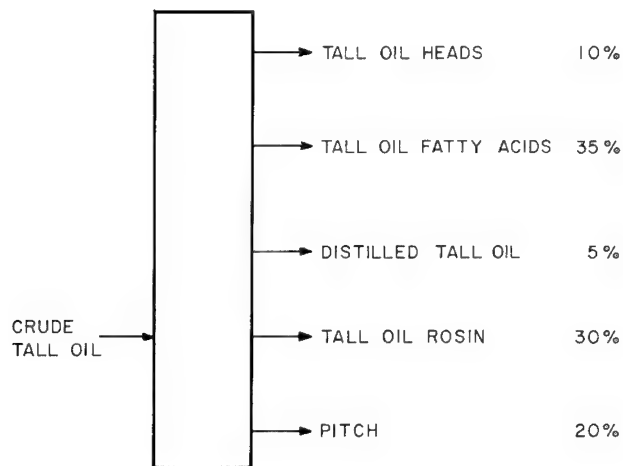
(SERIES OF DISTILLATION COLUMNS)

FIG. 1. Separation of crude tall oil.

pressures are essential within the columns. A good vacuum system is required to maintain these low pressures. Internal steam typically is used to assist in carrying the products up the columns.

The pitch or residue is often sold for fuel and as such, is wasted from a chemist's point of view. This pitch fraction is predominantly long-chain alcohol esters and sterol esters of fatty acids. Therefore, by allowing this esterification to take place one loses about 20% of the fatty acid present in tall oil as well as the sterols and other alcohols. Several processes for recovering these materials have been investigated, and one of the improvements that the industry can look forward to over the next few years is the improved utilization of this fraction.

UTILIZATION OF TALL OIL PRODUCTS

Basically the two products resulting from the refining of crude tall oil are fatty acids and rosin. In Table I the composition of the fatty acid fraction is shown. Figure 2 shows the formula of the three major rosin acids. Over 95% of the fatty acids and rosin acids in tall oil are unsaturated which means that for all practical purposes one has two reactive sites to work with in utilizing this material. In most applications the acid group is the important functional group but often the double bond plays an integral role, too. Of course, the use of fatty acids or oils to make soap easily predates the tall oil industry, but today one of the major uses for tall oil products is as a potassium soap in household and industrial cleaners. Also, the water-insoluble, heavy-metal soaps are used as paint driers. In fact, the protective coatings industry has been one of the largest consumers of tall oil for many years. Not only are the salts used to produce dryers, but also large quantities of the various acid fractions are used in combination with phthalic anhydride and polyalcohols to form the alkyd resin bases of many protective coatings.

TABLE I
Major Fatty Acids in Tall Oil

Palmitic Acid (C_{16} saturated)	1%
Stearic Acid (C_{18} saturated)	2%
Oleic Acid (C_{18} mono-unsaturated)	50%
Linoleic Acid (C_{18} di-unsaturated)	35%
Conjugated Linoleic Acid (C_{18} di-unsaturated)	8%
Other	4%

ABIETIC ACID   DEHYDROABIETIC ACID   PALUSTRIC ACID
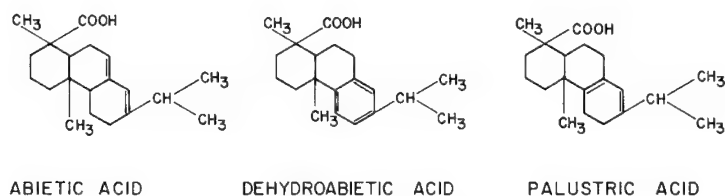
FIG. 2. Major rosin acids in tall oil.

Another major consumer of tall oil is the flotation industry. In the mining of most metals an impure rock is obtained which is purified through a series of floats. The rock is ground into a fine powder and then separated from the unwanted rock and sand by selectively floating one or the other in a frothing cell. Tall oil fatty acid salts often are used as the flotation reagents in anionic floats and, as such, play a major role in the production of such materials as phosphate fertilizers, phosphate-built detergents, and iron and steel products. The rubber industry uses salts of special stabilized tall oil fatty acids and rosin acids as the emulsifiers in emulsion polymerization of many different rubbers as well as poststabilizers for compounded foam latex. The tall oil products serve as an efficient emulsifier and upon acidification the rosin doubles as a tackifier, so that it is used widely in the production of styrene-butadiene rubber for tire production. In foam latex production for molded products and carpet backing, the fatty acid fractions normally are used as the emulsifier during polymerization and as a stabilizer during the compounding operation. The emulsification ability of various tall oil products also is utilized for preparing anionic asphalt emulsions.

In recent years, much of the rosin obtained as a by-product of the pulping operation has gone back to the paper producer in the form of rosin size. Size is added to the paper to impart water and ink resistance and thus is used in varying amounts with different grades of paper. Consequently, most paper producers are major consumers of rosin size. Over the years, as more efficient sizes have been desired, chemical modifications of rosin have been made to fill these needs.

The intermediate chemical area rapidly is becoming the major outlet for tall oil, and since this seems to be the direction the industry is emphasizing, the future for this route will be discussed in some detail. Intermediate chemicals is a vague term used to describe the many areas where either rosin or fatty acids are chemically modified or further processed prior to being incorporated into a product or used in the processing of some product—some examples would be: 1) Production of fatty amines from tall oil fatty acids; 2) Conversion to epoxidized esters for the plasticization and stabilization of polyvinyl chloride resins; 3) Their condensation with ethylene oxide to form detergents and general purpose surfactants; 4) Sulfation or sulfonation of the fatty acids to produce multipurpose surfactants and defoamers; 5) Esterification of fatty acids for utility in lubricants and textile processing acids; and 6) Esterification and dimerization of rosin for ink resins. In these and the many other applications where tall oil has become an essential chemical for performing a specific function, the industry is working to modify further its products to meet the growing needs of industry today.

DIMER ACID DERIVATIVES

Two of the rapidly growing areas for utilization of high-quality tall oil fatty acids involve their conversion to poly-basic acids. The first of these conversion processes became commercially important about 20 years ago. Now there are six producers of dimer acid, a C_{36} dibasic acid (Fig. 3), which has found its greatest utility in polyamide resins. Several hundred patents have been issued on the utilization of dimer acid and many articles have been written. Before the introduction of dimer acid there was no dibasic acid of greater chain length than C_{12}. This

$$HO-\overset{O}{\underset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-OH$$

AZELAIC ACID (C_9)

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH \overset{CH=CH}{\diagup} CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-OH$$

$$CH_2-CH$$

$$\underset{O}{\overset{\|}{C}}-OH$$

WESTVACO DiAcid (C_{21})

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-OH$$

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH-CH=CH-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-OH$$
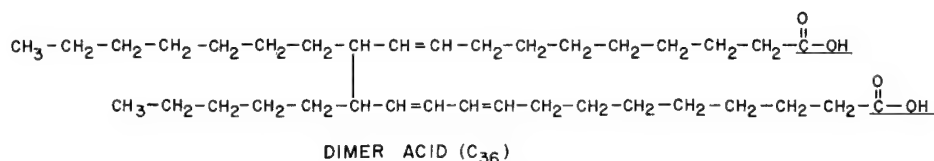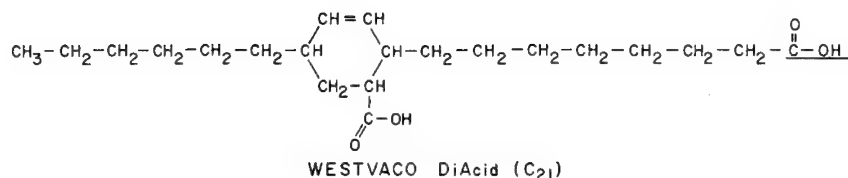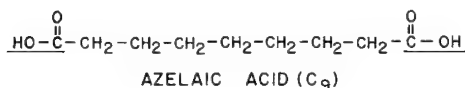
DIMER ACID (C_{36})

FIG. 3. Dibasic acid structures.

high molecular weight dibasic acid provided new opportunities for flexible poly-mers which easily found a home in the modern adhesives and coatings industries. Today, there are about 40 million lb of dimer acid produced with a sales value of some $20 million. The small amount of dimer that actually is used as the dibasic acid goes into metal working formulations to improve lubricity and provide corro-sion inhibition. Dimer generally is used as a chemical intermediate for making simple esters, polyesters, and polyamide resins. These derivatives have made their way into several major industries. Dimer esters are used as coatings modifiers to improve flexibility and impact resistance. They also find limited utility as special-ty plasticizers and lubricants. Approximately 75% of the dimer produced is used to prepare polyamide resins. General Mills pioneered in this area and controlled it until their patents expired about 10 years ago. There are now 12 to 15 domestic producers of polyamides, several of whom are basic in dimer acid production. There are three major types of polyamides produced from dimer acid: namely re-active, thermoplastic for adhesives, and thermoplastic for printing inks. The reac-tive polyamides are a condensation product of dimer acid and polyamines, typical-ly diethylenetriamine or triethylenetetramine. They are used as the curing resin or hardener for epoxy resins. Just as there are many varieties of epoxies, there are many different polyamide hardeners to match. Most are used in thermosetting surface coatings and in two component adhesive systems.

The thermoplastic polyamides fall basically into two major end-use categories. These are both made with dimer acid and ethylene diamine, but generally one is a moderate molecular weight polymer, whereas the other is a high molecular weight polymer. The high molecular weight polymer has been used extensively in the formulation of hot melt adhesives for the shoe industry. The other polyamides are used primarily in the production of flexible inks for printing on polyethylene pack-aging films. In its 20- to 30-year history dimer acid has made significant contri-butions in allowing the production of improved coatings, adhesives and inks. It must now be recognized as a well-established chemical specialty from a renewable source.

C_{21} DIBASIC ACID

The next major development in the dibasic acid field did not come until about two years ago when the Chemical Division of Westvaco Corporation introduced a C_{21} dicarboxylic acid. This product has proved to be an extremely versatile chemical, having properties very different from its closest sisters, the C_{12} and the C_{36} dibasic acids (Fig. 3). This new acid, Westvaco DiAcid 1550, is produced from tall oil fatty acids by condensing acrylic acid with the diunsaturated portion of the tall oil fatty acid using a Diels-Alder reaction [2]. This product, although on the market for only a brief time, has found use in a number of diverse markets. Obviously, it would be expected to make its way into the rapidly growing, dimer-based polyamide market. Excellent polyamide resins can be made from this C_{21} dibasic acid but these are often very different from the C_{36} varieties of polyamide resins. There are areas where either can be used, but generally this new acid is offering new opportunities for growth, produce improvement and diversification to the polyamide producer. The polyesters and simple esters of DiAcid also are interesting products with potential application in the textile lubricant, automotive lubricant and plasticizer areas. These esters can be used over very broad temperature ranges and, therefore, are naturals for use in areas where widely varying conditions must be tolerated. DiAcid amine salts and amides are excellent corrosion inhibitors in aqueous and petroleum systems and generally can be used in any of the areas where dimer acid is used.

The most unusual thing about this new C_{21} dibasic acid is that it is an excellent surfactant [3], finding utility as a general purpose emulsifier, a hydrotrope for phenolic disinfectants, a solubilizer and extender for nonionic surfactants in alkaline cleaners, a component of textile scouring formulations, a coupling agent for silicate-built heavy-duty laundry detergents, a major component of household fabric softeners, and a multifunctional component of floor polishes and surface coatings of all types. All of these industries are actively evaluating this dibasic acid in their research groups and plants.

The C_{36} dimer acid and the C_{21} DiAcid are two examples of diversification of the tall oil industry into specialty chemicals for diverse applications. I believe that the industry will move rapidly over the next few years to capitalize on its basic position in renewable chemicals to build an array of specialty chemicals which will serve most segments of industry. Beyond industrial chemicals, specialty chemicals from tall oil also have a future in food and cosmetics areas. In 10 to 20 years it may not be unreasonable to imagine trees being grown strictly as a source of renewable chemicals which play a major role in meeting the needs of the chemical, as well as the consumer, products industries.

REFERENCES

[1] Data are based on information obtained from the Pulp Chemicals Association and a profile of the industry in the *Chemical Marketing Reporter*, July 8, 1975.
[2] U.S. Patent 3,753,968.
[3] B. F. Ward and C. G. Force, *J. Am. Oil Chem. Soc.*, in press.

STRUCTURE, STEREOCHEMISTRY, AND REACTIVITY OF NATURAL CONDENSED TANNINS AS BASIS FOR THEIR EXTENDED INDUSTRIAL APPLICATION

DAVID G. ROUX, DANEEL FERREIRA, HANS K. L. HUNDT, and ELFRANCO MALAN

Department of Chemistry,
University of the Orange Free State,
Bloemfontein 9300, South Africa

SYNOPSIS

Condensed tannins of commercial importance are comprised of repeating flavan-3-ol units linked through 4,6 and terminal 4,8 bonds. The terminal unit invariably differs from the remainder in phenolic substitution. The tannins represent gradational mixtures falling mainly within the mass range 500–3000. Assessment of their structures and stereochemistry over the higher molecular range by means of physical methods presents difficulties due to complexity of the mixtures, compounded by rotational isomerism about the interflavonoid bonds. The repeating nature of the condensation has nevertheless been determined up to the tetraflavonoid level (M ~1100).

Knowledge of the composition and physical properties of those natural extracts in which tannins occur, of the organized structure of tannins, of the differential reactivity of their nucleophilic centers, and of their phenolic substitution has assisted in extending the scope of their industrial application to include a range of phenolic wood adhesives, precipitants and depressants. Other tannin reactions of potential industrial interest are briefly described.

The variety of successful applications developed hitherto underscores the versatility of condensed tannins as industrial raw material.

INTRODUCTION

Condensed tannins, in common with those flavonoids from which they are derived, are known for their ubiquitous distribution in nature and also for their substantial concentration in the heartwoods and barks of trees. Where these sources were found to be significantly rich, commercial development through large-scale afforestation and/or industrial extraction often followed, primarily for use in tanning. Production of tannins for this particular end-use reached its zenith during 1948–1950 and has since progressively declined. However, this factor coupled with the recent advent of the energy crisis has stimulated research on the broader industrial usefulness of tannins as condensed phenolics.

Applied research and development work in this direction may be approached

335

with success on an empirical basis, but is generally accelerated by basic chemical knowledge of tanning extracts.

THE CHEMISTRY OF CONDENSED TANNINS

Condensed tannins consist of flavonoid units which have undergone varying degrees of condensation, and tannins are invariably associated with their immediate precursors (flavan-3-ols, flavan-3,4-diols), other flavonoid analogues [1–5], carbohydrates, and traces of amino and imino acids [6]. Among these the simple flavonoid analogues provide direct clues as to the phenolic substitution present in the tannins, but it should be recognized that flavonoids and nitrogen-containing acids are present in concentrations which are too low to influence the chemical and physical characteristics of the extract as a whole. However, the simple carbohydrates (hexoses, pentoses, cyclitols, and disaccharides) and complex glucuronates (hydrocolloid gums) are often present in sufficient quantity to decrease or increase viscosity respectively, and excessive variation in their percentages would alter the physical properties of the natural extract independently of contributions related to the degree of condensation of the tannins.

Flavonoids and Flavonoid Interrelationships in Tanning Extracts. This group of compounds, commonly known as "phenolic nontannins," represents the most studied group among the commercially important tanning extracts because of their relative simplicity. They are comprised of flavan-3,4-diols (leuco-anthocyanidins), flavan-3-ols (catechins), dihydroflavonols (flavanonols), flavonols, flavanones, chalcones, and coumaran-3-ones {benzofuran-3[2H]-ones}, thus representing most of the known classes of flavonoid analogs [1–5].

Typical are those of black wattle ("Mimosa") bark extract (Scheme I) where the four possible combinations of resorcinol and phloroglucinol (A-rings) with catechol and pyrogallol (B-rings) coexist, although these flavonoids (1–15) constitute

A. Flavan-3,4-diols

(+)-leucofisetinidin (1)

(+)-leucorobinetinidin (2)

B. Flavan-3-ols

(−)-fisetinidol (3)
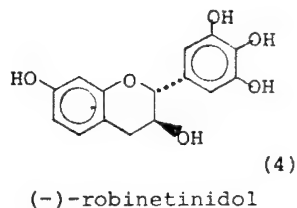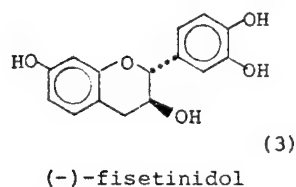
(−)-robinetinidol (4)

Scheme I. Flavonoid interrelationships in black wattle ("Mimosa") bark extract (*Acacia mearnsii*) [1–3].

(5)

(+)-catechin

(6)

(+)-gallocatechin

C. Dihydroflavonols

(7)

(+)-fustin

(8)

(+)-dihydrorobinetin

D. Flavonols

(9)

fisetin

(10)

robinetin

(11)

quercetrin
(R = rhamnose)

(12)

myricitrin
(R = rhamnose)

E. Flavanones

(13)

(±)-butin

F. Chalcones

(14)

butein

(15)

robtein
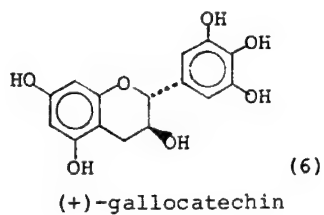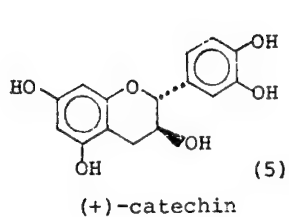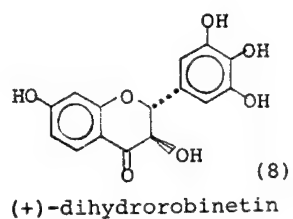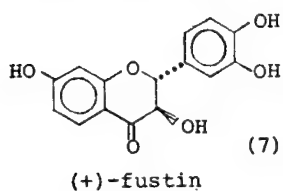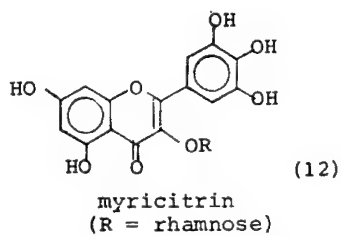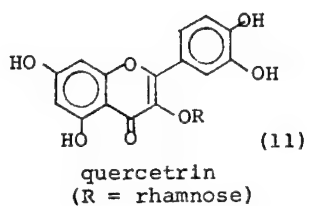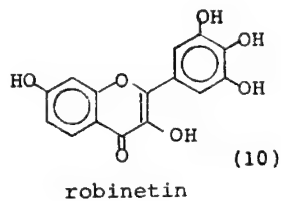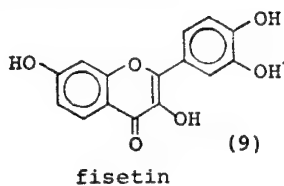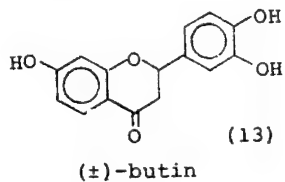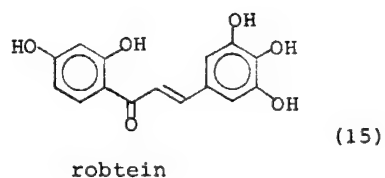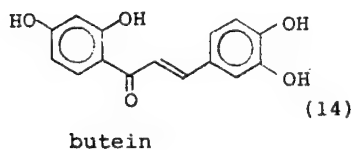
G.   Anthocyanidins generated from wattle tannins
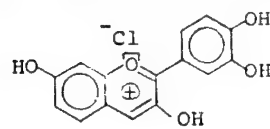
(16)

fisetinidin
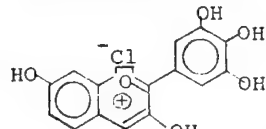
(17)

robinetinidin
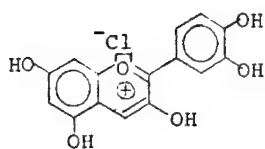
(18)

cyanidin
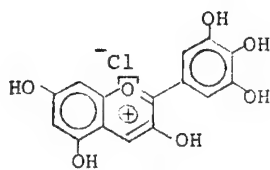
(19)

delphinidin

a very minor percentage (ca. 3%) of the total phenolics [3].   Significantly, each of the four combinations of phenolic substitution is to be found in black wattle tannins which yield the anthocyanidins, fisetinidin, robinetinidin, cyanidin, and delphinidin chlorides with 3 N HCl-isopropanol (1:4 v/v) under pressure (Scheme I).

Similar but less elaborate relationships apparently also exist in quebracho wood extract (Scheme II) which has, however, been studied in somewhat less detail (Schinopsis balansae and S. lorentzii)[4,5,7,8].

A.   Flavan-3,4-diols
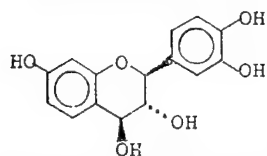
(20)

(-)-leucofisetinidin
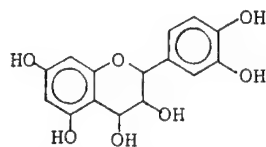
(21)

leucocyanidin

B.   Flavan-3-ols
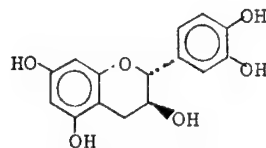
(5)

(+)-catechin

C.   Dihydroflavonols
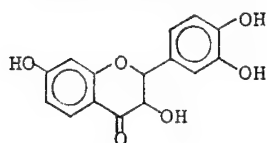
(7)

fustin

Scheme II. Flavonoid interrelationships in quebracho wood extracts (*Schinopsis balansae* and *S. lorentzii*) [4,5,7,8].

D. Flavonols[a]

(9)
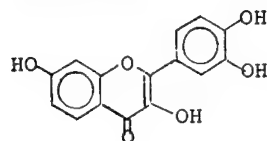
fisetin
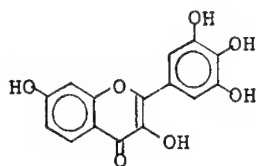
(10)

robinetin

E. Coumaran-3-ones[b]
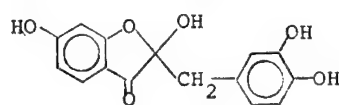
(22)

2,3',4',6-tetrahydroxy-2-benzylcoumaranone

[a] Together with 4'-O-methylfisetin and 4',7-dihydroxyflavonol
[b] Together with 4'-methoxy-2,3',6-trihydroxy-2-benzylcoumaranore
Fisetinidin cation (anthocyanidin)   (+)-Catechin

[4,5,7], only (−)-leucofisetinidin (20) [8], the flavonols, and 2-benzylcoumaran-ones [7] being isolated. The tannins furnish the anthocyanidins, fisetinidin chloride (16) and cyanidin chloride (18) which again reflect the main substitution patterns (cf. Scheme II) as in the case of black wattle extract.

Biflavonoids: The Condensation Aptitudes of Flavonoids. Among the above groups of monoflavonoids (Schemes I and II) only flavan-3,4-diols (type A) and certain flavan-3-ols (type B) apparently participate in tannin formation. This finding appears to be logical since carbonyl groups at the 4-positions (or their equivalent) in all the remaining compounds, not only strongly reduce the nucleophilic character of their A-rings, which militates against self-condensation, but also occupy one of the positions through which natural condensation occurs.

By contrast, the meta-substitution of resorcinol A-rings of the flavan-3,4-diols by hydroxyl and heterocyclic oxygen groups create strong nucleophilic centers at the 6- and 8-positions, and nucleophilic character is further enhanced by meta-trisubstitution as in (+)-catechin and (+)-gallocatechin (phloroglucinol A-rings).

Meta-disubstitution (and also meta-trisubstitution) with oxygen on the A-rings of flavan-3,4-diols (1), (2) also promotes formation of the equivalent of benzylcarbonium ions at the 4-position, which are stabilized by delocalization of the charge on a benzene ring with ortho- and paraoxygenated substituents.

Thus, from the aspect of linking these units (types A and B, Scheme I) to form biflavonoids which represent the first step in condensed tannin formation, (+)-catechin (5) and (+)-gallocatechin (6) offer the strongest nucleophilic centres, while (+)-leucofisetinidin (1) and (+)-leucorobinetinidin (2) provide potential benzylcarbonium ions for electrophilic substitution. Logically, attack on the catechins should be at the more accessible of the two centers on the A-ring, represented by the 8-position.

Presuming that condensation occurs via an ionic mechanism, the anticipated products based on mechanistic and steric considerations are in accord with those found among wattle tannins, namely (+)-leucofisetinidin-(+)-catechin (23), (+)-

leucorobinetinidin-(+)-catechin (24) and (+)-leucorobinetinidin-(+)-gallocatechin (25) [9].
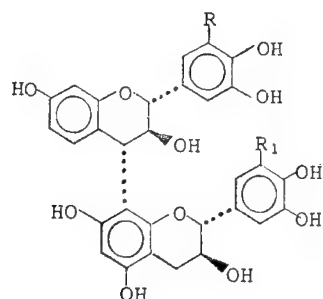
(23)   R=R$_1$=H
(24)   R=OH;   R$_1$=H
(25)   R=R$_1$=OH

Similar biflavonoid units which correspond to (−)-leucofisetinidin-(+)-catechin (26) have been isolated from the heartwood perimeter of *S. balansae* (quebracho) [10], but these exist as mixtures of rotational isomers which could not be resolved.
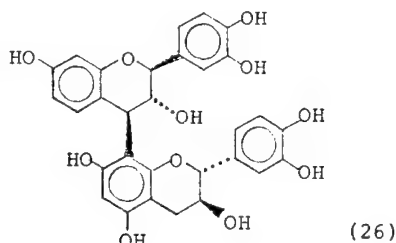

(26)

Similar association of flavan-3,4-diols, (+)-catechin and related biflavonoids exists in the woods of *Acacia luederitzii* [11], *A. giraffae* [12] and *Colophospermum mopane* [13].   These observations place an ionic mechanism in tannin formation almost beyond doubt.

Reactivity and Orientation in Electrophilic Substitution of Flavonoids.   The relative accessibility and/or reactivity of flavonoid units was examined by selective bromination with pyridine hydrobromide perbromide using units of the phloroglucinol and resorcinol series.   (+)-Tetra-O-methylcatechin (27) is brominated preferentially in the 8-position [14].   Only when this position is filled does substitution
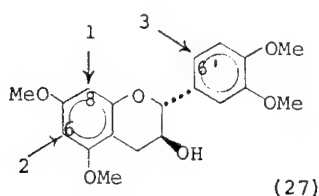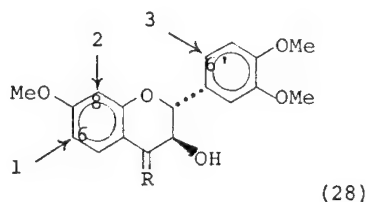
(27)   (28)

commence at the 6-position.   The B-ring is singularly unreactive, but with excess brominating agent a low degree of substitution at the 6′-position occurs.   The bromination sequence 8 > 6 ≫ 6′ for (+)-catechin tetramethyl ether is shown in (27) [14].   However, for the resorcinol equivalent, (−)-tri-O-methylfisetinidol

[(28) R = H₂] and also for (+)-tri-O-methylfustin [(28) R = O] the substitution sequence for the A-ring is modified to 6 > 8 ≫ 6′ as indicated [14]. Preferential 8- and 6-substitution in phloroglucinol and resorcinol type flavonoids, respectively, must presumably be related to the greater accessibility of these positions in each instance.

These preferential substitution effects which appear to be obeyed at the biflavonoid range find further parallels over the tri- and tetraflavonoid ranges.

Tri- and Tetraflavonoid Tannins. True affinity effects of polyflavanoids for collagen developed from the triflavonoid level (M ∼800) and thereafter increase rapidly with increasing mass [15]. These compounds may be regarded as true tannins.

Considering the multiplicity of diastereoisomers and rotational isomers theoretically possible at these molecular ranges, the problems of their separation become formidable. However, a triflavonoid condensed tannin (29) from the heartwood of the mopane (*Colophospermum mopane*) [13,16] and a tetraflavonoid unit (30) from the karree (*Rhus lancea*) [17] showed that the principle of condensation

(29)   (30)
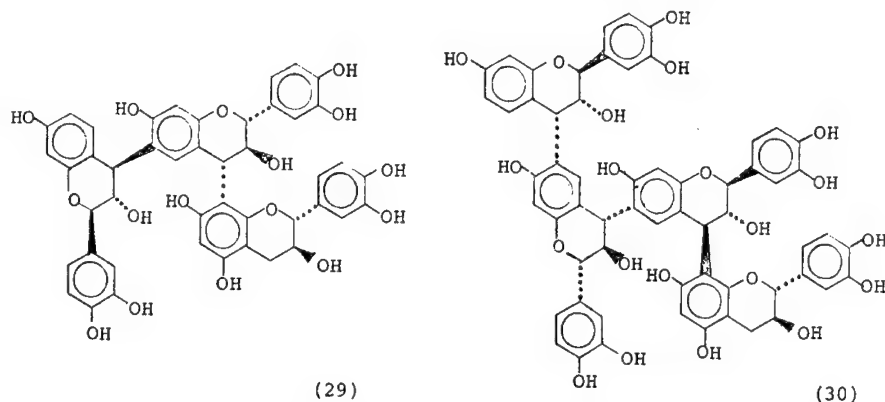
based on 4,6-links between resorcinol units, following initial 4,8-links between resorcinol and terminal phloroglucinol units, persists.

The recurrent 4,6-linkages between the "upper" units was demonstrated by NMR spectrometry (A-ring singlets) and by degradation where β-resorcylic (31) and 4,6-dihydroxyisophthalic acids (32) (and not 2,4-dihydroxyisophthalic acid)

(31)   (32)
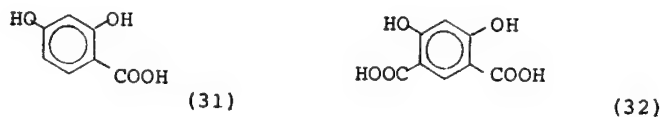
result [17], while the 4,8-linkage to terminal units is based on the interpretation of the shifts of all methoxyl NMR resonances during progressive C₆D₆ addition to CHCl₃ solutions of the methyl ethers of the tannins.

In both *C. mopane* and *R. lancea* the tannins, associated with others, are accompanied by the appropriate (+)- or (−)-leucofisetinidin and (+)-catechin "precursors."

Commercially afforested black wattle ("Mimosa") bark extract (*Acacia mearnsii*) gives evidence of a similar and continuing principle of condensation at the triflavonoid level, e.g. (+)-bileucofisetinidin-(+)-catechin, (+)-leucofisetinidin-

(+)-leucorobinetinidin-(+)-catechin and (+)-bileucorobinetinidin-(+)-gallocatechin amongst others [18].

In all instances as with the biflavonoids the more accessible 8-position on (+)-catechin provides the nucleophilic function of the terminal unit, while the electrophile is presumably represented by a 4-carbonium ion generated from the flavan-3,4-diol. Electrophilic substitution is repeated on the upper unit of the resultant flavonoid at the more accessible 6-position. In this way the principle of self-condensation may apparently be continued resulting in units as large as deca- and undecaflavonoids (M ~3000) for wattle tannins (number average mass 1250) and poliflavonoids of a higher average mass range (1784) for quebracho [19].

Phenolic Substitution and the Extremes of Condensation Aptitudes of Flavonoids in Tannin Formation. Notable is the observation that where phloroglucinol-type leuco-anthocyanidins populate plant extracts, the mixture consists almost entirely of highly condensed tannins. For example, the red mangrove wood (*Rhizophora mucronata*) extract consists predominantly of highly condensed leucocyanidin tannins (33) which readily yield cyanidin with mineral acid, accompanied by

(33)

(34)
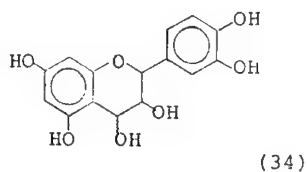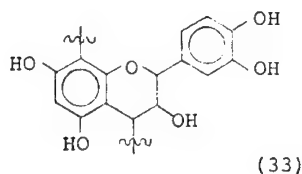
traces of a flavan-3,4-diol precursor (34) [20]. By comparison a vast range of *Acacia* heartwoods which contain high concentrations of melacacidin [(35) R = OH] and teracacidin [(35) R = H] diastereoisomers with pyrogallol A-rings exhibit negligible tannin content [12,21], and these compounds do not participate in condensation.

(35)
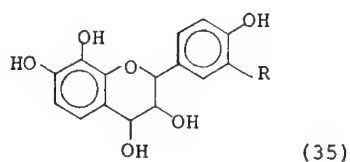
These phenomena may be rationalized on the basis that 4-benzylcarbonium ions of the phloroglucinol type represent the most stable (i.e. strong electrophilic) among those discussed, and the phloroglucinol A-rings simultaneously furnish the strongest nucleophiles. Conversely, the pyrogallol A-ring system in flavan-3,4-diols furnishes both the weakest electrophilic 4-carbonium ion and nucleophilic center. The combination of these factors is thus in each instance responsible for the relative extremes in tendencies for self-condensation, enzymic factors being neglected [12].

## THE REACTIVITY OF TANNINS AS REPEATING CONDENSATES

Considered as a high-molecular, natural "polymer" the condensed tannins exhibit many properties of individual flavan-3-ol units, but also a number of unique

reactions.   Knowledge of these is important in handling and industrial application of tannin extracts.

Hydrolysis and Condensation under Strongly Acid Conditions.   When heated in the presence of strong mineral acids, tannins are subject to two competing reactions.   One is degradative leading to anthocyanidin and catechin formation as illustrated for a typical biflavonoid (36), whereas the second is condensative as a re-

(36)

(+)-Catechin
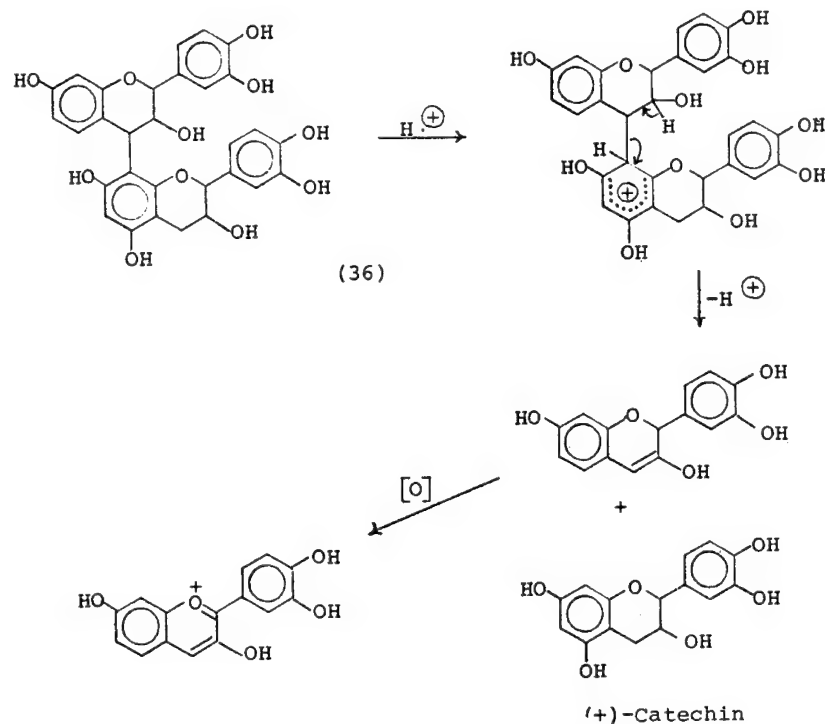
sult of hydrolysis of heterocyclic rings (*p*-hydroxybenzylether links).   The *p*-hydroxybenzylcarbonium ions (37) created condense randomly with nucleophilic centers on other tannin units to form "phlobaphenes" or "tanners reds."   Other

(36)

(37)

Substitution on poliflavonoids (tannins)

Phlobaphenes
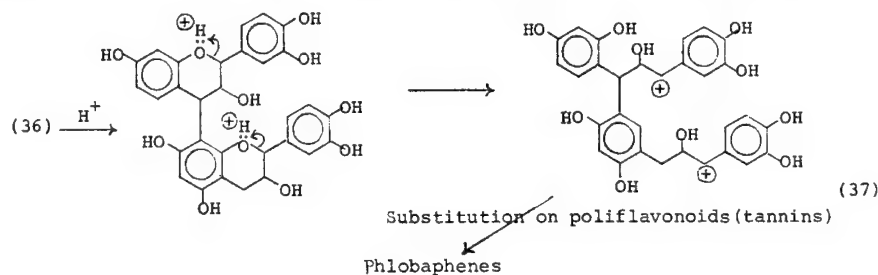
modes of condensation, e.g., free radical coupling of B-ring catechol units cannot be excluded in the presence of atmospheric oxygen.

Predominantly alcoholic conditions, e.g., 80%–100% EtOH, leads to a preference for hydrolysis and anthocyanidin formation, although self-condensation is not excluded, while under aqueous conditions phlobaphene formation, or formation of insoluble condensates, predominates.

In absolute alcohols, e.g., ethanol, n- and isopropanol partial etherification of the alcoholic 3-hydroxy groups occurs in the presence of mineral acid, leading to both the anthocyanidin and its 3-O-alkyl derivative in increased yields [22].

Hydrolysis of the interflavonoid link under these conditions occurs far more readily where both "upper" and "lower" units are of the phloroglucinol A-ring type, e.g., the polyleucocyanidin tannins of mangrove extract [20].

Oxidative Darkening and Photochemical Reddening. In common with all phenols, and especially vicinal-hydroxylated phenols such as catechol and pyrogallol, tannins and phenols undergo oxidation and oxidative darkening in solution or in the presence of moisture. Oxidation is at a minimum around pH 2.5, increases rapidly after 3.5–4.6 and is rapid under alkaline conditions or in the presence of oxidases (enzymes commonly found in plant material, e.g., bark). Oxidation in solution is completely inhibited by the presence of low concentrations of compounds which have a higher oxidative potential than the catechol or pyrogallol functional groups of tannins, e.g., sodium bisulphite or SO_2. Organic acids suppress the oxidation of tannins, and tannins are stable as spray-dried extracts of low (ca. 4–5%) moisture content.

Quite distinct from the above phenomenon, tannins tend to undergo reddening in both direct and indirect sunlight. The phenomenon apparently has a relatively long induction phase and develops rapidly thereafter [23]. The effect is consistent with the mechanism as outlined below for a triflavonoid [(38) R = H], although no direct chemical proof has as yet been provided.
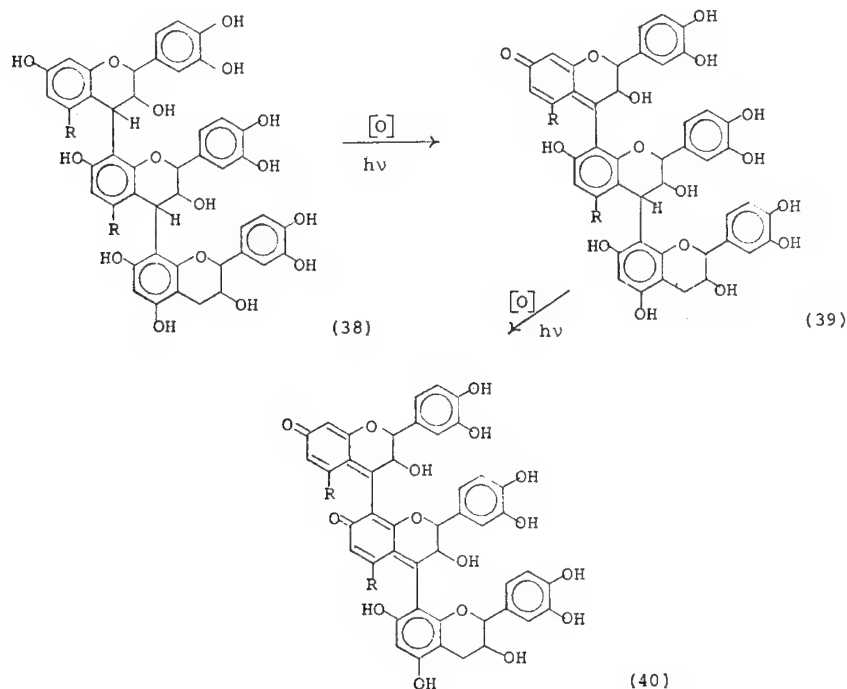
Thus, theoretically, after initial oxidation of an A-ring to a quinone methide (39) the mechanism [22] will repeat itself more readily (delocalization of radicals formed at C-4), leading to conjugated quinone methide chromophores. Additional hydroxylation at position 5 on the A-rings of the upper units [(38), (39), (40) R

= OH] will lead to a bathochromic (colour deepening) effect as is observed in the intense reddening of pholoroglucinol-type leucocyanidin tannins of mangrove bark extract [22].

Inhibition of reddening is possible by suitable choice of ultraviolet inhibitors of the o-hydroxybenzophenone type.

Tannins as Nucleophiles in Condensation with Formaldehyde: Reactive Centers. The well-known reaction of phenols with formaldehyde is either base- or acid-catalysed, weakly basic base-catalysed reactions being predominantly used in industrial applications. Increasingly alkaline conditions lead to progressive activation of the phenol as nucleophile, especially above pH 8 where phenoxide ion formation occurs.

In condensed tannin molecules the A-rings of the resorcinol (41) or pyrogallol (42) type of the constituent flavonoid units retain one highly reactive nucleophilic

(41)   (42)
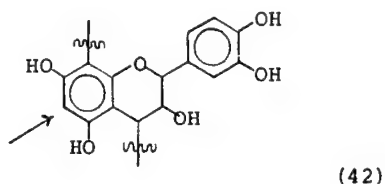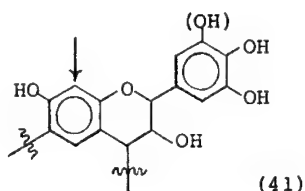
centre as indicated, the remainder accommodating the interflavonoid bond. Pyrogallol or catechol B-rings are by comparison unreactive, and may only be activated by anion formation at relatively high pH.

Accessibility of nucleophilic sites at positions 6 and 8 on A-rings (41, 42) during reaction with formaldehyde is unlikely to be inhibited by steric effects due to adjoining 7- (41) or 5- and 7-hydroxyl functions (42) or the bulk of the hydrated formaldehyde.

With only the latter as agent for crosslinking tannins via methylene bridges (43), the number of crosslinks will be limited by the relative immobility of the tannin molecules which restricts the probability of molecular juxtaposition suitable for bond formation. In general, low viscosity solutions of high concentration would favor multiple bonding, although these requirements are usually mutually excluding.

(43)
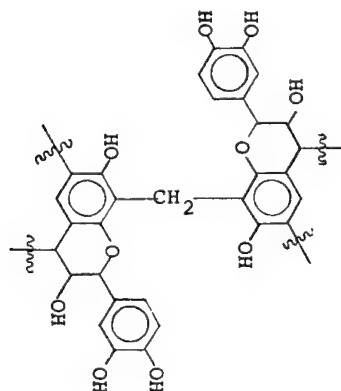
Absence of adequate crosslinks leads to the brittleness which is characteristic of many tannin-formaldehyde adhesives. This problem may be surmounted by adding phenol or resorcinol which not only lower viscosity by acting breakers of hydrogen bonds between the large tannin molecules, but which also assume positions between them, where with formaldehyde they readily provide mobile o- or p-hydroxybenzyl alcohol units favorable for crosslinking tannins. The dispersion of the phenolic units between tannins presumably limits their self-condensation during reaction with formaldehyde.

Sulfitation of Tannins with Sodium Bisulfite or Sodium Sulfite. Sulfitation presents one of the oldest but potentially most useful reaction in that it affects both the chemical and physical properties of tannins. The reaction is analagous to the sulfitation of lignins during pulping in that is solubilizes relatively insoluble tannins and reduces the viscosity of tannin extracts dramatically.

Based on previous work by Richtzenhain [24], the course of the reaction with flavan-3,4-diols and with catechin-like (flavan-3-ol) tannin units may be predicted (44) → (45); (46) → (47).
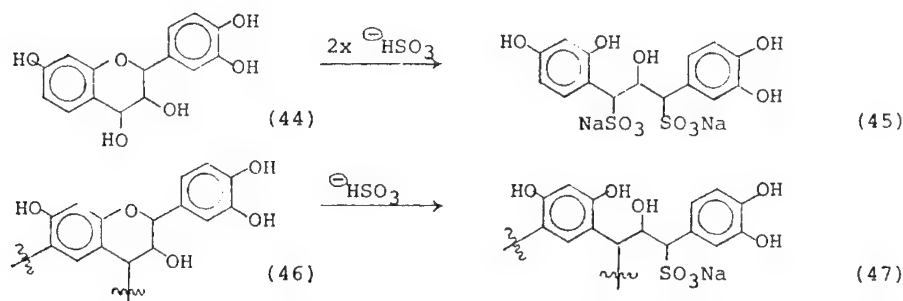
Introduction of the sulfonic group at the 2-position results in heterocyclic ring opening (i.e., hydrolysis of a benzyl ether link). Introduction of a polar group, as well as a phenolic hydroxyl, affords the enhanced solubility and assists in reducing viscosity. Treatment of quebracho extract with about 7% sulfite is, for example, required to give it adequate water solubility characteristics for tanning, the "ordinary" extract being soluble only in hot water. Other tanning extracts such as wattle ("Mimosa") and mangrove are readily water soluble.

The presence of sodium sulfonate groups in condensed tannins, while possibly affording the advantage of higher concentration of tannin phenolics in adhesive applications due to enhanced solubility, also represents a distinct disadvantage in that sulfonate groups promote sensitivity to moisture in the absence of adequate crosslinking.

Theoretically the displacement of sulfonic groups should be possible in the presence of strong alkali in a S_N2-type mechanism (48) → (49). However, it is likely
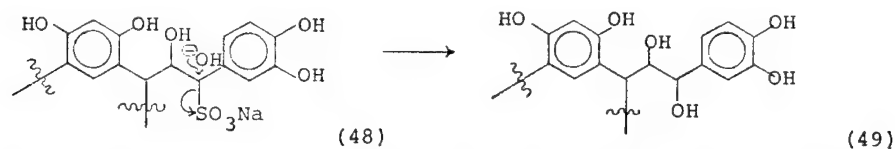
that the product will not only contain excess alkali (perhaps useful in adhesive applications), but also salts from the displacement reaction. Total replacement of the sulfonic group by hydroxyl, if feasible, would lead to a tannin in which the A-

ring phenolics (resorcinol or phloroglucinol) are more activated as a result of hydrolysis of the ether bridge of each flavonoid unit, and perhaps more readily available for reaction with formaldehyde because of generally increased mobility of the tannin molecule as a whole.

CHEMICAL ASPECTS OF INDUSTRIAL UTILIZATION OF CONDENSED TANNINS

From their recent chemistry, condensed tannins may now be considered to be biogenetically condensed flavonoid "polymers" suitable for some specialized industrial use or as replacement for phenols in many of their known applications in industry.

Production of tannin extracts has hitherto been geared to the requirements of the tanning industry, and new outlets may conceivably set different standards for specific end-uses. Some established applications and their requirements are outlined below.

Standardization of Natural Phenolic Extracts for Industrial Use

Industrial utilization sets varying standards of chemical and physical reproducbility, of which the following are currently applied to meet requirements of the tanning industry: 1) Standardized methods of afforestation, e.g., seed selection, espacement, thinning, and felling; 2) Harvesting of extractable material on a fixed rotation and sustained yield basis to ensure continued supplies or, less satisfactorily, harvesting a suitably cosmopolitan population of trees of different age groups from natural forests; 3) Consistent climatic conditions to ensure extracts which are free of, or low in the seasonal variation of components; 4) Standardized extraction procedures, e.g., countercurrent open-vat leaching at fixed time and temperature, or pressure leaching under similar conditions; 5) Standardized concentration procedures, e.g., evaporation of water in triple-effect vacuum systems for production of "solid" extracts, or preferably spray-drying to ensure ready solubility and low moisture content.

The tanning industry places high premium on low color values (low degree of oxidative discoloration), but neglects viscosity.

Amongst forestry-based industries which produce large tonnages of tannin extracts, at present only wattle (based on sustained afforestation of *Acacia mearnsii* in South Africa, Rhodesia, East Africa, India, and Brazil) and quebracho (based on natural forests of *Schinopsis balansae* and *S. lorentzii* in the Argentine and Paraquay) merit consideration. Mangrove bark extraction (from the swamp-growing tree *Rhizophora mucronata*) has completely declined due to cost of harvesting, while chestnut wood extract (*Castanea savita* and *C. dentata*) consists mainly of hydrolyzable tannins and does not fall into the category of condensed tannins.

Of the two important extracts, wattle is afforested scientifically on a 8–10 year rotation and the extract has natural solubility in water. A limited quantity of lightly sulfited wattle extract is produced as bleaching agent used only in finishing leather. Quebracho is derived from natural forests which are not reestablished. The trees reach maturity after 150–200 years and extract requires bisulfiting to

promote the required degree of water solubility. "Ordinary" (unsulfited) quebracho extract, which sludges in cold water, finds application in the final loading of vegetable leather.

Adhesive Applications of Condensed Tannins

Considering the high molecular, precondensed nature of tannins, the amount of formaldehyde required in their cold- and thermosetting adhesive applications is normally well below that required for the combination of making phenolic resoles from phenol and their setting.

A number of products and processes based on tannins are detailed below:

Generation of Resorcinol [25]. The flavonoid of black wattle wood, as distinct from those of wattle bark, consists predominantly of (+)-mollisacacidin [(1): (+)-leucofisetinidin] together with (−)-fisetinidol (3), (+)-fustin (7), fisetin (9), (±)-butin (13) and butein (14) in minor proportion [1]. They are associated in the heartwood with condensed tannins which are unique in that they possess flavan-3,4-diol terminal groups (50). Among these three biflavonoids [(50) n = 1] of differing stereochemistry have been characterized [26], together with a triflavonoid [(50) n = 2] [27] consisting of a mixture of diastereoisomers and/or rotamers. The tannin mixture ranges in mass up to 3000 [(50) n = 10] [19].

(50)
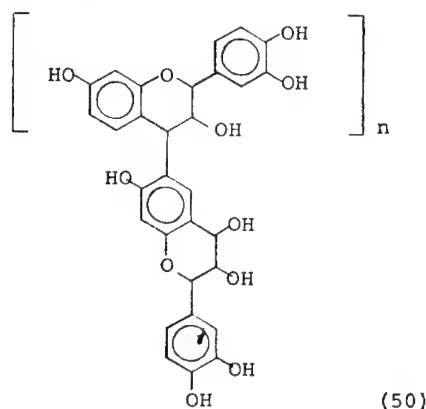
All compounds are accordingly based on resorcinol (A-rings) and catechol (B-rings) only, and alkali fusion of the wood extract as expected gives resorcinol (also β-resorcylic acid if its decarboxylation is not complete) and protocatechuic acid.

The wood contains about 8% extractives which afford 8% crystalline resorcinol on alkali fusion [24].

The economics of production centers around grinding and suitable extraction of the heartwood. This could provide an alternative source of resorcinol to the synthesis based on benzene.

## Cold-Set Wood Adhesive Applications Based on Wattle Bark Extract

Graft Condensation of Resorcinol [28]. Limited offering of formaldehyde to black wattle ("Mimosa") extract under weakly basic conditions leads to introduc-

tion of methylol groups, presumably at the remaining reactive centres on the A-rings of tannins (51). These tannin-formaldehyde resol intermediates are very re-


(51)
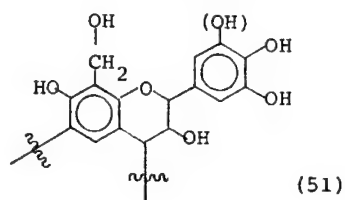
active, and in aqueous solution are subject to premature condensation with unsubstituted phenolic nuclei of other tannin units. This tendency is counteracted by forming the tannin resole in predominantly methanolic solution and reacting the intermediate (51) with a molar quantity of resorcinol [29]. This leads to the grafting of the reactive resorcinol to the flavonoid units of the tannin via a methylene bridge.

This grafted adduct (52) is stable and may be spray-dried without appreciable

(52)
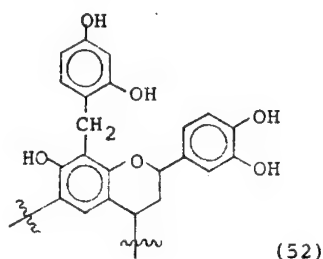
loss of reactivity. The grafted resorcinol units react with paraformaldehyde under typical cold-set conditions for the lamination of composite beams. The bonds are completely water-resistant and comparable in strength to cold-set resorcinol or phenol-resorcinol adhesives.

Resorcinol as Direct Bridging Agent [30]. The problem associated with linking a percentage of the highly reactive nucleophilic center on the A-ring of each flavonoid unit in tannins has already been mentioned (see Tannin Reactivity) and is of special importance in cold-set applications where activation through heat or upward adjustment of pH is not applicable. The problem may be solved by introducing a phenol, resorcinol, which serves as strong bifunctional electrophile after reaction with formaldehyde (53) → (54), and enables bridging of some of the less

(53)   (54)
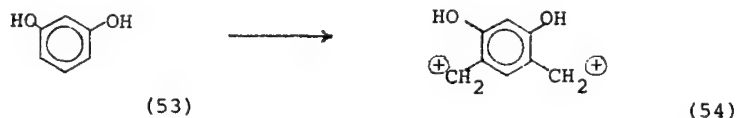
strong nucleophilic centers on the tannin molecule (55). Appropriate dispersion of resorcinol among tannin molecules limits its self-condensation through methylene bridges.

Thus, an appropriate mixture of wattle tannins and resorcinol with active (low polymeric) paraformaldehyde gives an adhesive with excellent cold-set properties.
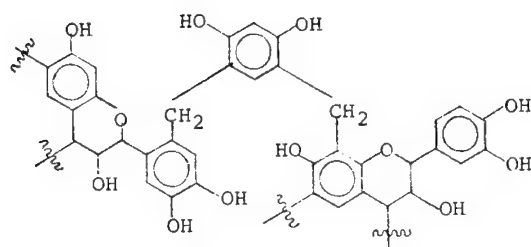
(55)

Thermosetting Wood Adhesive Applications Based on Wattle Bark Extract

Chipboard Applications [31]. Low viscosity is the prime requirement of natural tannin extracts in an application which involves spraying of chips with a high percentage solids (50%–60%) adhesive. The presence of sulfonic groups as in sulphited extracts is detrimental to the cold-soak characteristics of chipboard and this excludes sulphiting as a method of viscosity-reduction.

The relatively low viscosity of wattle ("Mimosa") extract is contributed partly by sugars which act as hydrogen-bond breakers; by the relatively low degree of condensation of tannins (number average mass 1250) and by a suitably high degree of hydroxylation (predominantly resorcinol + pyrogallol nuclei) which promotes solubility.

The low inherent viscosity of wattle extract may be lowered by addition of phenolic hydrogen-bond breakers (e.g., phenol itself) or simply by selection of the extraction procedure or temperature. Thus open-vat leaching (a simple countercurrent process) gives extracts of lower viscosity than the more modern pressure leaching on the same phenolic basis.

In chipboard adhesive applications the presence of phenol is needed not only for viscosity reduction, but for assisting crosslinking of tannins with paraformaldehyde during thermosetting.

Chipboard used primarily as weatherboard, and also as shutterboard and based on a wattle extract adhesive is in current manufacture in South Africa. The wattle-based chipboard has the advantage of lower swelling characteristics than comparable phenol-formaldehyde based products, and also improved stability to weathering.

Plywood Applications. Wattle-based formulations in this thermosetting application are essentially the same as the above, but without undue emphasis on the low viscosity requirement of the tannin extract—although this property is always advantageous.

The tendency towards brittleness of the bond in the product is overcome by suitable fortification with phenol or phenol-resorcinol admixtures—thus increasing the relative degree of crosslinking of tannins, and by suitable choice of fillers of which wood flour and cocoanut shell flour have been shown to be most effective for wattle-based adhesives.

Satisfactory "pot-life" for practical open and closed assembly times is achieved by pH-adjustment in relation to the activity of the paraformaldehyde used, and the quality of the final bond. Formulations must be adjusted according to the type of veneer and the requirements of the pressing cycle.

A phenol-resorcinol fortified wattle extract developed by the Forest Products

Laboratory, C.S.I.R.O., Melbourne has been in use in the Australian plywood industry for nearly ten years.

Corrugated Cardboard Adhesive [32]. Wattle bark extract with formaldehyde successfully replaces resorcinol-formaldehyde in admixture with starch in this thermosetting application. Adhesives of this type are applied where corrugated cardboard containers must withstand damp due to condensation when removed from cold storage.

This application has recently been developed in South Africa.

Flocculant for Clay Suspensions in Water Treatment [33]

Strongly acid conditions are used to link ethanolamine with wattle tannins in a Mannich-type reaction (56) → (57) to form amphoteric tannins (57) which are water soluble.
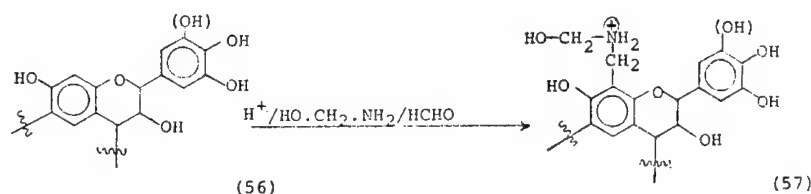
The amphotannins have been used in South Africa for over 15 years as flocculant for clay suspensions in municipal water treatment. In this process no residual salts or ions remain in the treated water, the amphotannins combining with the suspended clay and coprecipitating.

Calcite Depressant in Ore Flotation [34]

Unmodified wattle bark extract is used as depressant for unwanted calcite in the recovery of fluorspar in South Africa by a single mining firm. Consumption is currently 100 tons per month, and the extract is applied at 2 lb tannin per ton of low grade (20%–25% CaF_2) ore.

Quebracho has also been used in this application.

Foundry Core Binders

Foundry cores of high strength have been produced using both hot and cold-setting tannin-formaldehyde adhesives. The wattle tannin-formaldehyde resol [see (50)], which may be prepared and stored in the solid form, reacts with more extract (when mixed in the proportion of 1:3) under the influence of heat at stoving temperatures up to 170°C.

In cold-set applications setting of the resol with resorcinol may be acid-catalysed with ammonium chloride and p-toluene sulphonic acid. Setting of cores from the cold-setting mix can be accelerated at any time by stoving.

Bentonite Mud Conditioner in Oil Well Drilling [32]

Sulphited quebracho extract has been traditionally used as mud-thinning agent in shallow drilling. However, new criteria of stability and anticorrosive action at elevated temperatures have been introduced in recent years. With this in mind an effective conditioning agent for bentonite muds has been developed by incorporation of chrome salts into wattle extract. The product known as Kr6D is effective down to 6000 feet under normal drilling conditions and in the absence of high salinity.
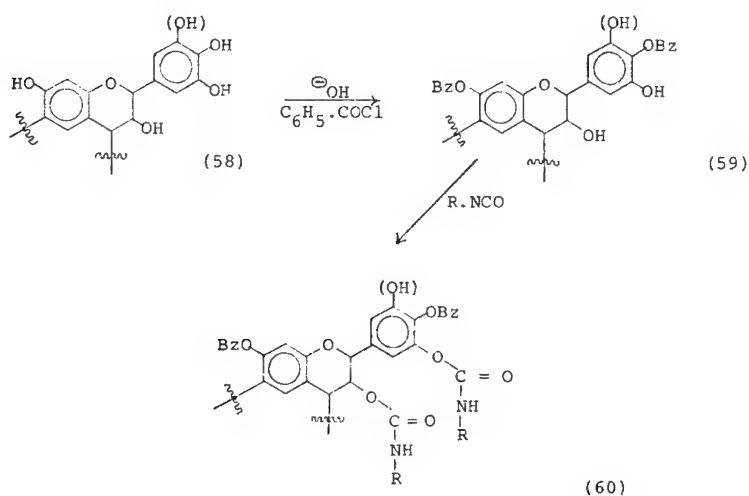
Polyurethane Surface Coatings Based on Wattle Tannins [35]

Surface coatings of the polyurethane type with good resistance to weathering have been developed from diisocyanates with partially benzoylated Mimosa tannins as hydroxyl source.

Partial benzoylation of tannin units by the well-known Schotten-Baumann method (58) → (59) serves a variety of purposes: 1) the number of hydroxyl groups per flavonoid unit is reduced, thus limiting reactivity with the isocyanates; 2) partially benzoylated tannins, prepared from the extract, readily precipitate leaving unreacted carbohydrates in aqueous solution; 3) partial benzoylation confers solubility on the highly polar tannins in those mutual systems (e.g., cyclohexanone-butyl acetate; cyclohexanone-methyl ethyl ketone-acetone; or cyclohexanol-methyl ethyl ketone-acetone-ethyl acetate-turpentine) required for reaction with diisocyanates; 4) introduction of benzoyl groups in slight excess of two per flavonoid unit promotes colour stability, indicating that substitution particularly of the A-ring should be ensured to avoid formation of quinone-methide chromophores [see (23)].

The bifunctional diisocyanates serve to crosslink tannin units (60) producing films of high gloss and scratch resistance, and also stability to sunlight when applied to wood surfaces. However, the tannin presents the lowest cost component in the final product.

CONCLUSIONS

While condensed tannin extracts have been used for manufacturing vegetable-tanned leather since the turn of the last century, extension of their industrial use mainly to adhesives, precipitates, depressants and viscosity agents reflects recent development. These uses have contributed to the consumption of significant tonnages of extract, and emphasized their importance as industrial raw materials relative to synthetic phenols based on petroleum.

Future development should be accelerated by chemical knowledge of both tannin extract composition and "polymeric" tannin structure.

REFERENCES

[1] D. G. Roux, *Tydskrif vir Natuurwetenskappe,.* 139 (1970).
[2] D. G. Roux, *Phytochemistry, 11,* 1219 (1972).
[3] S. E. Drewes and D. G. Roux, *Biochem. J., 87,* 167 (1963).
[4] H. G. C. King and T. White, *J. Soc. Leather Trades' Chem., 41,* 368 (1957).
[5] D. G. Roux and E. Paulus, *Biochem. J., 78,* 785 (1961).
[6] H. M. Saayman and D. G. Roux, *Biochem. J., 97,* 794 (1965).
[7] H. G. C. King, T. White, and R. B. Hughes, *J. Chem. Soc.,* 3234 (1961).
[8] J. W. Clark-Lewis and D. G. Roux, *J. Chem. Soc.,* 1402 (1959).
[9] S. E. Drewes, D. G. Roux, H. M. Saayman, S. H. Eggers, and J. Feeney, *J. Chem. Soc., C,* 1302 (1967).
[10] F. du R. Volsteedt and D. G. Roux, unpublished work.
[11] I. C. du Preez, A. C. Rowan, and D. G. Roux, *Chem. Comm.,* 492 (1970).
[12] E. Malan and D. G. Roux, *Phytochemistry, 14,* 1835 (1975).
[13] I. C. du Preez, Ph.D. Thesis, University of the Orange Free State, South Africa (December, 1971).
[14] H. K. L. Hundt and D. G. Roux, unpublished work.
[15] D. G. Roux, *J. Soc. Leather Trades' Chem., 39,* 80 (1955).
[16] I. C. du Preez, A. C. Rowan and D. G. Roux, *Chem. Comm.,* 315 (1971).
[17] D. Ferreira, H. K. L. Hundt and D. G. Roux, *Chem. Comm.,* 1257 (1971).
[18] H. M. Saayman, unpublished work.
[19] D. G. Roux and S. R. Evelyn, *Biochem. J., 76,* 17 (1960).
[20] D. G. Roux, unpublished work.
[21] M. D. Tindale and D. G. Roux, *Phytochemistry, 13,* 829 (1974).
[22] D. G. Roux and M. C. Bill, *Nature, 183,* 42 (1959).
[23] T. G. Fourie, Ph.D. Thesis, University of the Orange Free State, South Africa (January 1975).
[24] H. Richtzenhain and B. Alfredsson, *Ber., 89,* 378 (1956).
[25] D. G. Roux and D. Ferreira, unpublished work.
[26] S. E. Drewes, D. G. Roux, S. H. Eggers, and J. Feeney, *J. Chem. Soc., C,* 1217 (1967).
[27] S. E. Drewes and D. G. Roux, *Chem. Comm.,* 1 (1968).
[28] Developed by Mr. D. Gray, Leather Industries Research Institute, P.O. Box 185, Grahamstown 6140 in collaboration with Mr. A. G. D. Ryder and Dr. A. Pizzi, Bondtite Adhesives (Pty) Ltd., P.O. Box 877, Port Elizabeth 6000, and the senior author.
[29] T. White and E. Knowles, "Use of Mimosa and Quebracho Tannins in Adhesive Manufacture", Forestal Land, Timber and Railways Co. Ltd., Shell-Mex House, Strand, London W.C.2, England.
[30] Developed by Dr. A. Pizzi, Bondtite Adhesives (Pty) Ltd., Port Elizabeth 6000 in collaboration with the senior author.
[31] Developed initially by Novobord Ltd., P.O. Box 1371, Port Elizabeth 6000 and improved by the Bondtite Adhesives group.
[32] Developed by Dr. H. M. Saayman, Leather Industries Research Institute, Grahamstown 6140.
[33] Developed by the Natal Tanning Extract Co., P.O. Box 39, Pietermaritzburg 3200.
[34] Developed by Marico Flourspar, Zeerust 2865, Transvaal (subsidiary to U.S. Steel).
[35] S. E. Drewes, *Plastics, Paint and Rubber, 53* (1961); H. M. Saayman, *J. Oil and Colour Chem. Assoc., 57,* 114 (1974).

ON THE POSSIBILITIES OF USING BARK DURING AND AFTER BIOLOGICAL CONVERSION

A. ALESTALO and O. KOISTINEN

Enso-Gutzeit Osakeyhtiö, Research Centre, Imatra, Finland

SYNOPSIS

For several years now, investigations have been made to determine the effectiveness of using bark as a biofilter material to destroy the malodorous compounds of some pulp mill condensates. The promising results of these experiments made at the laboratory and pilot plant levels have led to the composting experiments. Bark has been used as a litter in dry toilets, hen houses, cow stalls, and in swine houses. As well as serving as a good litter material, bark has shown an excellent capacity to contain and to destroy the bad odors associated with human and animal wastes. After the bark and animal wastes are mixed, a biological action converts the mixture into a compost. The heat which evolves from this process has been found to be sufficient to kill pathogenic bacteria and the eggs of parasites. This compost has been used with good results in some preliminary fertilizing experiments.

More recently, investigations have been made into the possible uses of bark as a source of energy. Several alternative uses for bark have been compared in theoretical calculations to the use of bark as a conventional fuel.

INTRODUCTION

The search for good methods to utilize bark began in the 1960s when barking moved from the forest to the mills. At first, most of the bark which collected at the mills was disposed of by dumping. However, because of the high costs involved and the large areas required for dumping, this method of bark disposal is unsuitable. Many mills are now using bark as a fuel in power boilers. However, because moist bark has a low heat value, and because the investment costs for a bark boiler and stack gas cleaning equipment are relatively high, the combustion of bark can be considered primarily a wasteful method.

When one considers that the ash content of bark is roughly 10 times as great as that of stem wood, and that the amount of stem wood is roughly 10 times that of bark, it is evident that the removal of both bark and wood from the forests will double the nutrient losses from forest lands. From an ecological viewpoint, the investigations [1,2] to compost bark to obtain a fertilizer product were therefore very encouraging. The production of bark humus on the basis of these and other such investigations has, however, so far been relatively small, and the utilization of

355

bark humus has been restricted mainly to horticulture. The global shortage of food, the scarcity of agricultural land, the losses of agricultural land to roads and buildings, and the rapidly increasing population of the world have changed the situation drastically. The need to increase food production and to recycle the nutrients contained in the world's abundant organic wastes has led to the idea to compost bark with such wastes.

The Utilization of Bark in Biofilter

The basic construction and operation of the biofilter is shown in Figure 1, in which the filtering medium is bark. In our experiments, such a bark biofilter was used to purify malodorous pulp mill condensates. The effectiveness of this process depends upon the ability of the microorganisms living on the bark to oxidize the malodorous sulfur compounds to odorless forms and to reduce Biological Oxygen Demand (BOD) primarily by means of oxidizing methanol.
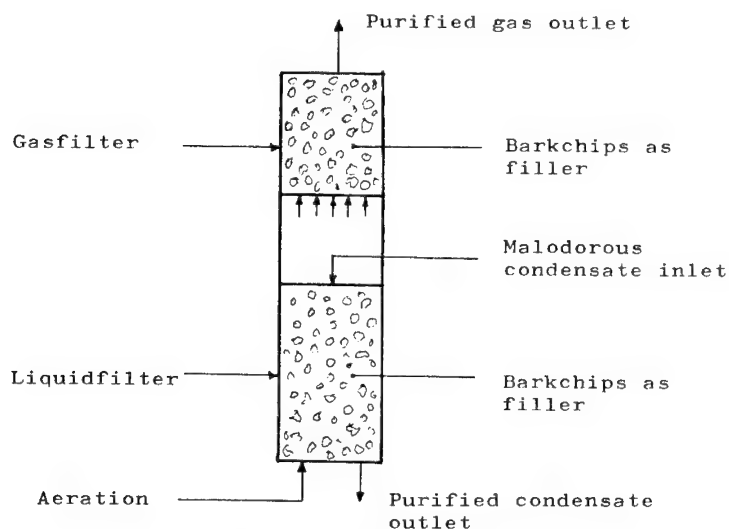

FIG. 1. Design of bark biofilter.

To intensify the oxidizing action of the various microorganisms, the bark medium was preimpregnated with nutrients. The oxygen necessary for the process was blown through the biofilter from bottom to top countercurrent to the flow of trickling condensate. Experiments made on the pilot plant level indicate that the efficiency of the bark biofilter in the oxidation of malodorous sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) is 90%–100%, and in the oxidation of methanol 40%–80%.

THE COMPOSTING OF BARK WITH TOILET WASTES

The good odor retaining capacity of bark (or its deodorant properties) found in our biofilter experiments led to the idea of the biological toilet system based on the

CONVENTIONAL

SYSTEMS BASED ON THE COMPOSTING
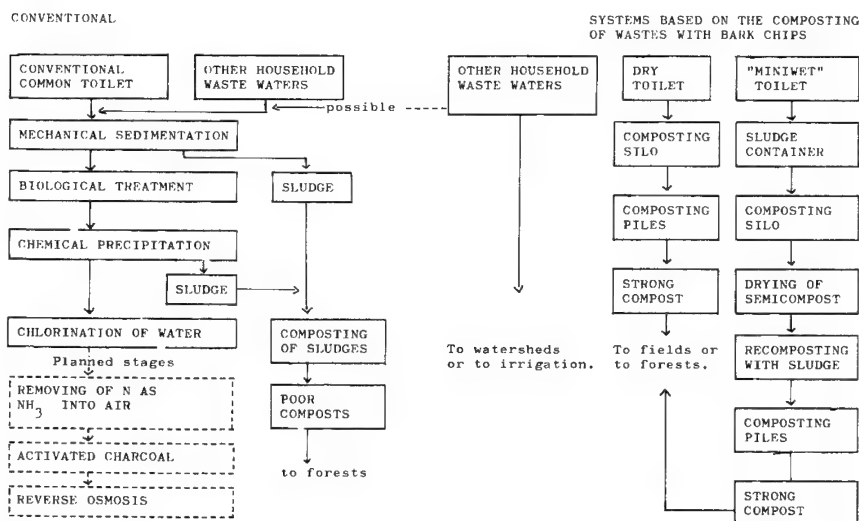OF WASTES WITH BARK CHIPS

FIG. 2. Comparison of waste water treatment systems.

utilization of bark as a litter. The first experiments were made at some summer cottages in 1971. Since then, such experiments have been enlarged and we now estimate that over 1000 people have tested this system and were pleased with the results. During our observations of the bark litter dry toilet, neither bad odors nor flies were noticed [3]. However, such a toilet system would appear to be practical only for use in one floor dwellings. For those houses with many floors and for collective purposes, the "miniwet" water toilet may be more practical. This type of toilet requires only 0.5 l.–1.2 l. per flush as compared to the 10 l.–15 l. per flush required by the conventional water toilet.

A schematic comparison of the conventional waste treatment system with a bark based system is shown in Figure 2. Compared to the conventional wastewater treatment system, the biological dry toilet system: 1) saves about 80 l.–100 l. per person-day of prime quality water; 2) produces a compost product which may be used directly as a fertilizer in agriculture and forestry; 3) all but eliminates the problem of contamination, of the sludge with the toxic elements lead, cadmium, and mercury [4]; and 4) helps to retain most of the nitrogen contained in the wastes.

COMPOSTING BARK WITH ANIMAL WASTES

The details of some cow waste experiments made in the stalls of 19 cows in December 1973, and of the beginning of some swine waste experiments are described in a previous article [3]. In short, the results of the experiments indicate that bark as a litter has a good capacity to reduce the bad odors associated with animal wastes. During the experiments, in fact, the bad odor problem was all but eliminated.

During the experiments with swine, one unexpected observation was made. For the first few days the sows and the baby pigs ate much of the bark litter. For the next few months, only one sow was provided with a bark litter. This sow continued to eat bark for one to two months but then only nibbled at the bark. Perhaps
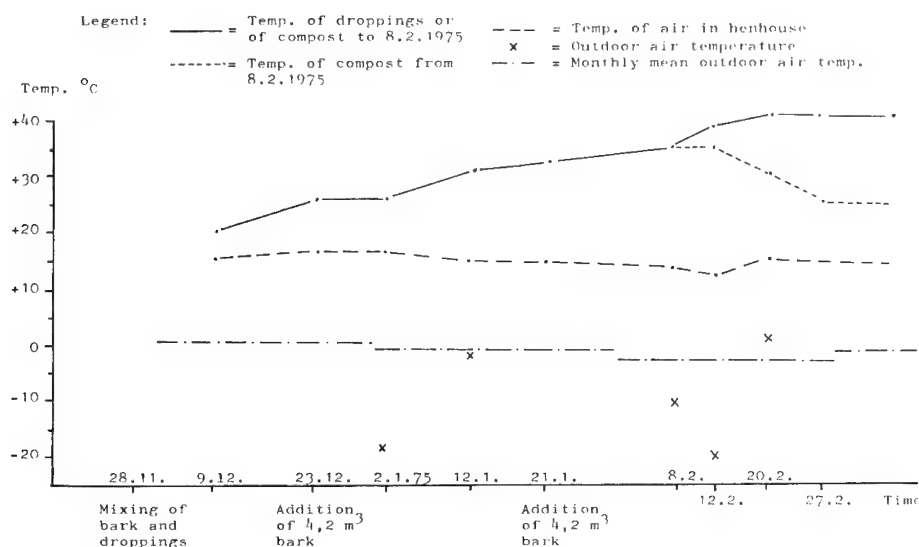
FIG. 3. Composting experiment in coop henhouse from November 11, 1974 to March 8, 1975.

the swine ate the bark to complement their diet with those trace elements not found in the mixed complete fodder. It was noticed that the first litter born to a bark-fed sow looked healthier than normal, so the bark litter experiment was continued, using three sows. By the end of March 1975, these sows had given birth to seven litters, all healthier looking and better in structure than normal.

During the preliminary chicken waste experiments, dry bark was used as a litter [3]. Since November 21, 1974, however, moist bark (35% dry wt) has been used as a litter. The moist bark litter experiment was made in a hen house which has a floor area of 150 m^2 and space enough for 1800 hens in two-story coops. However, only 960 hens were living in this building during the experiment. At the beginning of the experiment, 6 m^3 of moist bark was spread on the floor area below the occupied coops (48 m^2). During the experiment, temperature measurements were taken periodically. The data are shown in Figure 3. The results of this experiment confirmed the following:

1. The savings in building heating costs were Fmk 800 ($230.00).

2. The odor in the hen house had been reduced considerably.

3. The deodorant properties of the bark litter made the job of cleaning and treating chicken wastes more pleasant.

COMPOSTING BARK WITH KITCHEN FOOD WASTES

As in previous waste experiments [3], the object of this experiment was to determine whether or not kitchen wastes could be composted with bark to yield a useful fertilizer product. By producing such a product, the nutrients and organic matter contained in household wastes and bark could easily be reclaimed for use in agriculture.

To make use of the good deodorant properties of bark, bark chips were sprinkled, as required, on the top surface of the wastes in the household waste bins. The full waste bins were then emptied into a silo for completion of the composting.

Not only did the deodorant properties of the bark make the job of handling the wastes more pleasant but it also served to make the malodorous wastes less attractive to flies. This last point could be important because flies attracted to household wastes can also spread pathogenic bacteria throughout the household. In addition, when large enough quantities of wastes (2 m^3) are composted with bark chips, high enough temperatures (60°–80°C) are generated in the compost pile to disinfect the wastes.

THE EFFECTIVENESS OF BARK COMPOST AS A SOIL IMPROVER AND FERTILIZER

In agriculture, bark humus products have been used effectively to maintain the spring moisture in clay soil. Using bark humus in this manner, wheat harvests have been increased 100% over harvests of controls during normal and dry summers. On the basis of such experiments [5], it is presumable that bark composts would also be effective in maintaining moisture in clay soils. Because the weather had been exceptionally rainy and moist in Finland, the harvests from our compost experiments were only 8%–11% more than that of the control. However, the crop production level was high. Depending upon which of the three bark composts was used, the wheat harvests varied between 6,240 and 6,390 kg/ha.

As can be seen in Table I, bark composts have a high micronutrient content. In many places where effective agriculture has been dependent upon the use of commercial fertilizers, there may be a critical shortage of micronutrients. This shortage may eventually dminish the harvest or lower the quality of the crops.

TABLE I
Composition of the Bark Chips and Bark Composts

Material		Bark chips	Bark composts			
		24.04.1973	Cow stall 20.9.74	Swinery 26.9.74	Dry toilet 11.10.74	Henhouse 10.3.75
Ash	%					
	total	4,10	16,10	14,40	17,90	23,40
	soluble	2,50	11,20	10,10	12,70	18,90
N	g/kg	4,15	21,30	25,60	27,00	30,90
P	"	0,39	8,03	7,42	12,60	19,60
K	"	1,17	18,20	15,40	13,40	16,90
Ca	g/kg	7,02	26,30	20,40	30,10	50,50
Mg	"	0,72	4,54	5,33	4,94	5,85
S	"	0,89	4,10	4,50	4,35	6,08
Fe	"	0,60	1,42	3,08	2,45	1,83
Mn	mg/kg	390,00	448,00	590,00	530,00	585,00
Cu	"	5,00	40,00	156,00	32,00	85,60
Zn	"	115,00	225,00	544,00	440,00	459,00
Mo	mg/kg	1,60	16,00	13,00	18,00	24,30
Co	"	1,30	7,10	6,10	4,30	10,30
B	"	7,80	14,70	19,90	17,10	17,20
Se	"	0,02	0,05	0,18	0,17	0,28
Na	g/kg	0,15	3,57	3,40	6,34	4,54
Cl	"	0,32	9,08	6,13	8,17	6,90
C	%	53,30	46,60	47,60	45,60	42,60
C : N : P		129:1:0,1	22:1:0,4	19:1:0,3	17:1:0,5	14:1:0,6

TABLE II
The Effect of Bark Compost Fertilization on the Growth of Trees

The species of tree and compost treatment	Length of tree cm		Length growth cm/year			DBH mm Autumn	Changes in 1974	
	Spring	Autumn					DBH growth mm	Cross-section increase cm²
	1972	1974	1972	1973	1974	1974		
Siberian larch								
No 1. June 1973 DTBC	209	530	123	100	98	57,3	15,9	12,35
No 2. " "	150	300	21	64	65	25,3	6,4	2,25
No 3. April 1974 SBC	187	237	13	9	28	19,1	6,4	1,59
No 4.	164	201	16	11	10	12,7	3,1	0,55
Grey alder								
No 1. June 1973 DTBC		427		153	122	31,8	11,1	4,58
No 2.		337		101	102	22,3	6,3	1,91

Legend: DTBC = Dry toilet bark compost added 10 liters
SBC = Swinery bark compost added 10 liters
All trees were fertilized in the spring of 1972 with a basic nitrogen,
phosphorous, potassium fertilizer.
DBH = Diameter at breast height

The results of the preliminary tree fertilizing experiments are shown in Table II. These data indicate that bark compost may be an effective fertilizer for use in forestry. Because the number of experimental trees was small, however, and because the time of the experiment was relatively short, the positive results cannot be said to be statistically significant.

One possible reason for the increase in tree growth may be related to the previous shortage of trace nutrients in the soil. The idea that bark composts contain all the necessary trace elements required for good tree growth is supported by the results of some tree fertilization experiments made with wood ash. One such experiment was made in some swamps in Finland over a period of about 30 years [6]. In this experiment, the annual growth of the trees increased to 9–10 m³/ha, about 3–4 times the average rate of growth in Finland. In another such experiment, the rate of growth of those trees which had been fertilized with wood ash was greater than that of trees which had been fertilized with the same amount of commercial K and P fertilizer. Of course the small pH changes induced in the soil by the alkaline wood ash may have had some effect upon the increased rate of growth observed. Nevertheless, the results of both bark compost and wood ash fertilizing experiments indicate that micronutrients are important for good tree growth.

Evidence indicates that wood ash can be used to treat swamp soils rich in organic matter and poor in nutrients for greatly improved tree growth. If bark composts cannot all be used in agriculture, why not use the composts to condition those forest soils which are poor in organic matter and nutrients? Because they contain some antagonistic microorganisms [7], bark composts used as a soil conditioner could also help to control plant diseases.

BARK IN ENERGY PRODUCTION

From the results of some preliminary hen house waste experiments made during the mild winter of 1974–75, it was calculated that the savings in heating costs gained by using moist bark as a litter were about 12 times as great as the savings in fuel costs which could be gained by burning moist bark in a boiler. Where the

TABLE III

A Theoretical Estimation of the Solar Energy Absorbed by Snow Which has Been Dusted with Bark Compost Powder.

GIVEN: -   Solar radiation in Southern Finland (Latitude $61°$ N)

                      February: about 2 $kcal/cm^2$ (mean temperature $-7,8°C$)

                      March: "   6 "   (mean temperature $-4,4°C$)

                      April: "   8 "   (mean temperature $+2,3°C$)

ASSUMPTION: -   Dusted snow melts by April 10th or 10 days earlier than normal.

CALCULATIONS: -   During the 10 snow-free days gained by dusting the snow,

                     the solar radiation is $\frac{10 \text{ days}}{30 \text{ days}}$ x 8 $kcal/cm^2$ = 27 000 $kcal/m^2$

               -   Because bare soil will absorb 80 % of the energy but snow-covered soil will absorb only 20 %, the energy gained = 60 % x 27 000 $kcal/m^2$ = 16 000 $kcal/m^2$.

               -   The energy which would be gained by burning the dry bark portion of the compost powder required for dusting is,

                          60 g (bark)   4 000 kcal/kg = 240 kcal.

CONCLUSIONS: -   The energy acquired in this manner is about 70 times greater than the energy which would be acquired by burning bark in a boiler.

more expensive dried bark must be used to serve as an effective litter, such big savings in building heating costs could not be expected. However, bark compost made from the wastes of any animal could be used to recycle nitrogen back into agricultural land, thus saving the energy required to manufacture nitrogen fertilizers. Certain high-yield plants such as alder and red clover may be grown rapidly without nitrogen fertilization but they may not grow well in soils which are poor in certain micronutrients. If bark composts were used to grow such high-yield plants in place of those plants which require nitrogen fertilization, then there would be no need to consume such nonrenewable energy resources as oil to manufacture nitrogen fertilizers.

In those areas near the growing boundaries of certain plants, for example at the northern limits for the growing of wheat or trees in Finland, the lengthening of the growing period by several days might greatly increase plant growth. Such a lengthening may be made in the early spring by dusting the snow with a material which will absorb enough solar energy to accelerate the melting of snow [8]. Because it is dark in color and low in specific weight, bark compost powder may serve well as a dusting material. A theoretical estimation of the solar energy absorbed by snow which has been dusted with bark compost powder is described in Table III.

The scope of this paper does not allow for a complete assessment of the value of bark in composting compared to its value as a fuel. However, on the basis of the evidence gathered so far, it appears that the value of bark in composting is much greater than its value as a fuel. The nutrients and especially the micronutrients reclaimed from wastes by bark composting are necessary not only for growing plants but also as part of a complete diet for the promotion of health in animals and humans alike.

REFERENCES

[1] O. Isomäki, *Paper and Timber, 5,* 349 (1967).

[2] N. E. Virkola, Inlägg vid SPCI Bark Symp. Stockholm, Nov. 21, 1972.

[3] A. Alestalo and O. Koistinen, *ISWA, Inf. Bull.,* in press.

[4] K. Valdmaa, *Compost Sci. 5,* 23 (1974).

[5] G. Larpes, a paper presented in the "Miljövernseminar," Nordisk Jordbruksforskers Förening, Mattby, Sweden, Oct. 20, 1973.

[6] O. Huikari, Koetuloksia metsäojitettujen soiden lannoituksesta. Metsäntutkimuslaitoksen suontutkimusosaston tiedonantoja, Finland, Jan. 1973.

[7] C. Y. Hong and A. Ueyama, IUFRO Symp., Norway/Sweden, July, 1972.

[8] K. Arnold, in "Geology of the Arctic," G. E. Raagh, Ed., University of Toronto Press, p 989.

THE POLYPHENOLS FROM LOBLOLLY PINE BARK

P. FANG and G. D. McGINNIS

Forest Products Utilization Laboratory,
P.O. Drawer FP,
Mississippi State University,
State College, Mississippi 39762

SYNOPSIS

Loblolly pine bark contains a large amount of polyphenolic materials which can be extracted with 1% sodium hydroxide. The chemical and physical properties of these materials were found to be dependent on the conditions of the extraction. Extraction in the presence of oxygen gave a 36% yield of material which contained 44% oxygen. When the extraction was done under nitrogen, the yield was 18% and the material contained 39% oxygen.

Functional group analyses showed both types of polyphenols contained less than 2% methoxyl groups. These two alkaline-extractable polyphenols were further characterized by UV and IR spectroscopy. Methylated and acetylated derivatives were prepared, and their molecular weights were determined using high-pressure gel permeation chromatography and vapor-phase osmometry. Thermal decomposition properties were studied by thermogravimetry and pyrolytic gas chromatography. The results indicated that the polyphenolic material extracted under nitrogen was more thermally stable and gave more phenol products in which pyrocatechol predominated during pyrolysis. Programmed pyrolysis from 200°C to 600°C showed that the distribution of products was strongly influenced by the pyrolytic temperatures.

INTRODUCTION

The bark of many conifers is rich in extractable polyphenolic materials. These materials include the tannins, the phlobaphenes and the phenolic acids. All of these polyphenols are believed to be made up of similar structural units. Work by previous investigators has suggested that monomeric flavonoids and leucoanthocyanins are the precursors that yield, in turn, the tannins, the phlobaphenes, and still higher molecular weight polyphenols which resist extraction by neutral solvents [1-4].

The majority of the work on polyphenols in the United States has been done with western conifer barks, particularly western hemlock and Douglas fir. Very little research has been published on the chemistry of southern pine bark. Only

three studies, namely a study on the structure of the phenolic acid from slash pine bark [1], an analysis of the chemical constituents of loblolly pine bark [5], and a study of the water-soluble polyflavonoids in shortleaf pine outer bark [6], have been published concerning the chemistry of the polyphenols in southern pine bark. The lack of knowledge of the structure and reactions of this material has been a hindrance to the effective utilization of this material. At present only a minimal amount of this material is being utilized.

In this study, the polyphenols were obtained by alkaline extraction of extractive-free loblolly pine bark, the extract was characterized by various spectroscopic methods.   The molecular weights were determined using high-pressure liquid chromatography and vapor-phase osmometry, and the thermal decomposition patterns were determined using thermogravimetric analysis and pyrolytic gas chromatography.

EXPERIMENTAL

Isolation of Polyphenols

Extractive-free loblolly pine bark (20 g) was vigorously stirred with 1 1. of 1% NaOH solution under a nitrogen atmosphere at room temperature for 72 hr, after which the sample was immediately filtered and deionized with ion exchange resin Rexyn 101 (H$^+$) under nitrogen.   The aqueous solution was evaporated to dryness under reduced pressure at 45°–50°C.   The solid sample was placed in a vacuum oven at 105°C for 24 hr to remove most of the associated water [7-9].   An 18%

TABLE I

Yields and Properties of the Polyphenols Extracted from Loblolly Pine Bark[a]

Polyphenol	Extraction Condition	Yield	Sol.	Elemental Composition		
				C%	H%	O%
I	1% NaOH Nitrogen	18%	DMSO	55.69	4.85	39.4
II	1% NaOH Oxygen	36%	DMSO H$_2$O	51.92	3.77	44.3

[a] Based on the oven-dried extractive-free bark.

yield of the resulting dark-brown amorphous material Polyphenol I was obtained. Polyphenol II was isolated using the same procedure as described above, except the extraction was done under oxygen.   A dark-brown material was obtained in a yield of 36%.   Elemental analyses of both polyphenols are shown in Table I.

Methylation of Polyphenols

The methylation was carried out using a procedure previously reported by Erman and Lyness [1]. Polyphenol I (3.0 g) was dissolved in 100 ml of dioxane-water (4 to 1) and treated with alcoholic diazomethane over a two-day period. The resulting solution was evaporated to dryness under reduced pressure. The solid material was redissolved in chloroform-methanol (4 to 1). Filtration and evaporation of the solution gave 2.3 g of methyl Polyphenol I. Methyl Polyphenol II (2.5 g) was obtained by following the same procedure. The two methylated polyphenols were subjected to acetylation.

Acetylation of Polyphenols

Following the procedure previously reported [1], the sample of polyphenol (1.0 g) was acetylated using 20 ml pyridine and 20 ml acetic anhydride. After the reaction was completed, 0.52 g of chloroform-soluble acetyl Polyphenol I was obtained which contained 25.4% acetyl group. Following the same procedure, 0.10 g of acetyl Polyphenol II containing 17.54% acetyl group was obtained.

Acetylation of Methyl Polyphenols

The methyl polyphenols obtained from methylation of polyphenol were treated by the same procedure as described above to obtain chloroform-soluble acetyl methyl polyphenols in quantitative yield. Functional group analyses gave the following results: Polyphenol I—Methoxyl, 9.75%; Acetyl, 14.16%; Polyphenol II—Methoxyl, 17.84%; Acetyl, 13.82%.

Titration of Hydroxyl Group

An indirect titration method was used by dissolving 30 mg samples in 35 ml of 0.1 N of $NaHCO_3$ or 0.1 N NaOH solution and then titrating with 0.1 N of HCl solution [10]. A Corning pH meter was used to indicate the end point of the titrations which were repeated three times for each sample.

Instrumentation Analyses and Molecular Weight Determination

The absorption spectra were obtained with samples containing about 20 mg/l of material in a 1 cm cell using a Beckman DB-G spectrophotometer. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer model 257 infrared spectrophotometer. The molecular weights of the phenolic derivatives were determined by high-pressure gel permeation using a Waters Associates liquid chromatograph (model 201/401) with chloroform as the solvent. The columns contained CPG-10-75, controlled porosity beads from Electro Nucleonics, Inc. The columns were standardized using polystyrene from Waters Associates. Vapor-phase osmometry was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, along with the elemental and functional group analyses.

Pyrolysis of Polyphenols

Thermogravimetric analyses (TG and DTG) were performed with a Perkin-Elmer TGS-1 model thermal analyzer, under programmed temperature at 10°C/min and 60 ml/min of nitrogen flow rate. A 1 mg sample was used for TG and a 5 mg sample for DTG.

Pyrolytic gas chromatography was conducted using a Fisher/Victoreen 27259 model pyrolyzer between 200°C and 600°C at intervals of 50°C. Using 10 mg samples under nitrogen, the pyrolysis products were swept to a Perkin-Elmer 900 gas chromatography system with an OV-17 column for separation and characterization. Pyrolyses of polyphenols were also conducted in a glass apparatus under 4 mm Hg initial vacuum, by raising the temperature for 4 hr to a maximum of 400°C. Products were collected in an air condensor and two traps cooled at −30°C for further identification.

Identification of Pyrolysis Products

Columns used in vapor-phase chromatography for the identification of phenols were OV-17, polyphenyl ether (5 ring), Carbowax 20 M and SE-30. Porapak Q was used for the identification of the low molecular weight decomposition products. Identification of the compounds was made by the comparison of retention times. Table II lists the relative retention time (phenol = 1.0) of phenols.

TABLE II
Relative Retention Times of Phenols

Column	OV-17	Polypheny Ether (5 ring)	Carbowax 20 M	SE-30
Temperature °C	65-210	65-200	65-200	70-225
Program rate, C/min	8	8	8	24
Flow rate, ml/min	40	40	60	40
Column length, ft	18	6	12	6
Time for phenol, min	0	8	27	3
Phenol	1.00	1.00	1.00	1.00
Guaiacol	1.26	1.35	0.87	---
o-Cresol	1.16	1.14	1.00	---
m,p-Cresols	1.20	1.27	1.11	---
2,6-Dimethylphenol	1.26	1.43	0.89	---
2,4-Dimethylphenol	1.37	1.48	1.10	---
3,5-Dimethylphenol	1.43	1.55	1.21	---
Creosol	1.48	1.60	0.97	1.57
Catechol	1.60	1.68	---	---
4-Methylcatechol	1.79	1.92	---	---
Resorcinol	1.79	1.85	---	1.79
p-Hydroxybenzoic acid	---	---	---	1.81
Phloroglucinol	---	---	---	2.44

TABLE III

R_f Values for Phenols Separated by TLC on Silica Gel Sheet

	R_f		
Compound	Benzene: Acetic acid 8/1	Benzene	Benzene: Acetic acid: 8/1/0.5
Phenol	0.59	0.32	---
Guaiacol	0.62	0.55	---
o-Cresol	0.62	0.42	---
m-Cresol	0.56	0.32	---
p-Cresol	0.53	0.31	---
2.4-Dimethylphenol	0.58	0.41	---
2.6-Dimethylphenol	0.62	0.58	---
3.5-Dimethylphenol	0.54	---	---
Creosol	---	0.52	---
Catechol	0.26	0.05	0.59
4-Methylcatechol	0.31	0.05	0.64
Resorcinol	0.13	0.02	0.44
p-Hydroxybenzoic acid	0.37	0.02	0.49
Phloroglucinol	0.01	0.01	0.18

Quantitative determinations were made mainly by vapor-phase chromatography using the integrated peak areas for calculation. p-Hydroxybenzoic acid was determined by comparing the intensity shown on TLC with the authentic sample.

Vapor-phase fragmentation was done by following the technique developed by Levy and Paul [11]. The individual compounds were separated on a GC system and transferred to a gold pyrolysis reactor (T = 700°C) (Chemical Data System, Inc., model 1200). In the reactor, the compounds were thermally fragmented, and the fragments were characterized through a second gas chromatograph. An OV-17 column was used for the first GC and Carbowax 20 M was used for the second GC. The pyrolysis products were identified by the comparison of the thermal dissociated fragments with the authentic samples. Thin-layer chromatography was conducted on Eastman Silica Gel Chromagram Sheets. For the identification of monohydroxy phenols, benzene was used as the solvent, and acetic-benzene-methanol was used for the case of dihydroxy phenols. Table III lists the R_f values obtained.

RESULTS AND DISCUSSION

Isolation and General Characterization

There are a variety of different methods for isolating polyphenols from bark [1,5,12,13]. In this study, the polyphenols were isolated from extractive-free bark by extraction with 1.0% sodium hydroxide under two different atmospheres, nitrogen and oxygen. It was found that the yields of the products, as well as the overall physical and chemical properties, were affected by the extraction atmosphere (Table I).
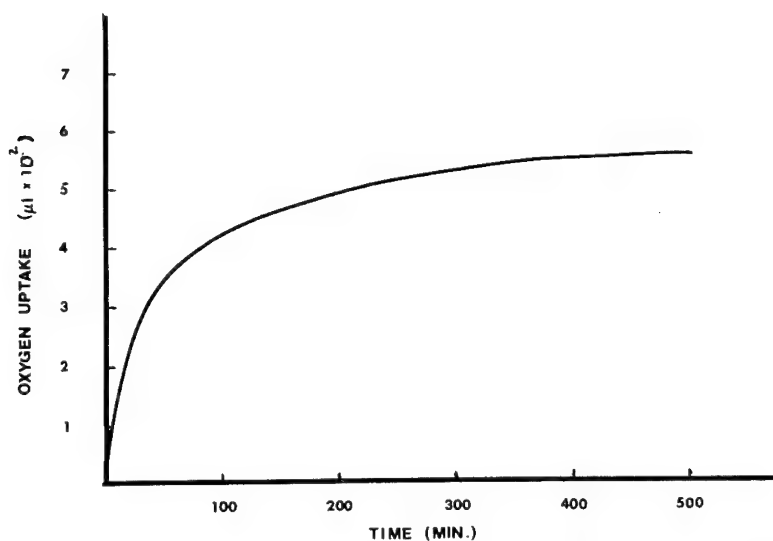
FIG. 1. Progress curve for the oxygen absorption of extractive-free loblolly pine bark in 1% NaOH solution at 27°C.

An 18% yield of alkaline-extractable material was obtained under nitrogen. This dark-brown amorphous material (Polyphenol I) was not soluble in water but was soluble in dimethyl sulfoxide and various aqueous organic solvents of acetone, methanol, or dioxane. The carbohydrate content was found to be 12%. Elemental analysis indicated 55.69% carbon, 4.85% hydrogen, and 39.4% oxygen. In contrast, a 36% yield of material was obtained during extraction under oxygen. This dark-brown material (Polyphenol II) was soluble in water, dimethyl sulfoxide, and in a variety of aqueous organic solvents. Elemental analysis showed that it contained more oxygen (44.3%) and less hydrogen (3.77%) and carbon (51.92%) than Polyphenol I. The carbohydrate content was 9%, which was less than that in Polyphenol I. The extraction under oxygen was also investigated using a Gilson respirometer. It was found that during the extraction, the polyphenols were reacting with molecular oxygen (Fig. 1). Samples of bark material (10 mg) in 1% sodium hydroxide absorbed 5.5×10^2 μl of oxygen in about 6 hr. Oxygen was apparently oxidizing the polyphenol and changing its chemical and physical structure. These results also indicate that there are two types of polyphenols in the bark. The first type is soluble in 1% sodium hydroxide, while the other type is only soluble in 1% sodium hydroxide in the presence of oxygen.

Functional group analyses (Table IV) indicated that both types of polyphenols contained very few methoxyl groups (1.70% and 1.81%). These results, plus the negative color reaction of both polyphenols with phloroglucinol-hydrochloric acid, indicated that lignin was not present [14].

The percentage of acidic groups was determined by titration with 0.1 N NaOH solution. It was found that Polyphenol I contained 10.0% acidic groups (calculated as acidic-hydroxyl groups) while Polyphenol II contained fewer acidic groups (7.1%). The titration was also done using sodium bicarbonate in order to determine the number of carboxylic acid groups. Polyphenol I was found to contain 3.5% acidic groups and Polyphenol II contained 5.1%. Under this condition the phenolic hydroxyl group, such as that found in catechol, did not react with sodium

TABLE IV
Functional Group Analyses of the Polyphenols Extracted from Loblolly Pine Bark[a]

Polyphenol	Methoxyl, %	Acidic Hydroxyl, % Carboxylic[a]	Total[b]
I	1.81	3.5	10.0
II	1.70	5.1	7.1

[a]Determined by titration with o.1 N NaHCO$_3$.
[b]Determined by titration with 0.1 N NaOH'

bicarbonate.   The titration method has been used previously to determine the phenolic groups in lignin and lignin derivatives [15–19].

The infrared spectrum of Polyphenol I showed a broad absorption for phenols (2.9–3.0 and 7.9–8.5 μ region) and a weak absorption for the carbonyl group (5.8–5.9 μ).   The spectrum of Polyphenol II was very similar, except the carbonyl band at 5.8–5.9 μ was much stronger.

The ultraviolet and visible absorption of Polyphenols I and II and of the two model compounds, catechin and polycatechin [4,7], in neutral solvents, dilute sodium hydroxide, and in AlCl$_3$-ethyl alcohol solutions, are shown in Figures 2–4. The λmax at 279 mμ present in the ultraviolet spectra of Polyphenol I indicates that there is no further conjugation with the 3,4-dihydroxy benzene system [1]. In addition, the aluminum chloride complex of Polyphenol I showed no bathochro-
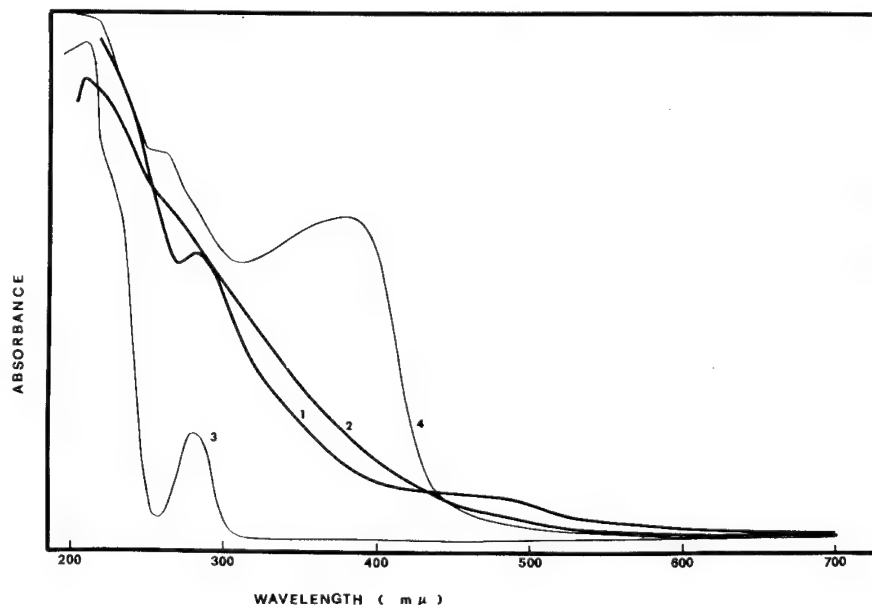
FIG. 2. Absorption spectra of (1) Polyphenol I, (2) Polyphenol II, (3) catechin, and (4) polycatechin in 95% EtOH-10% dioxane (9:1).
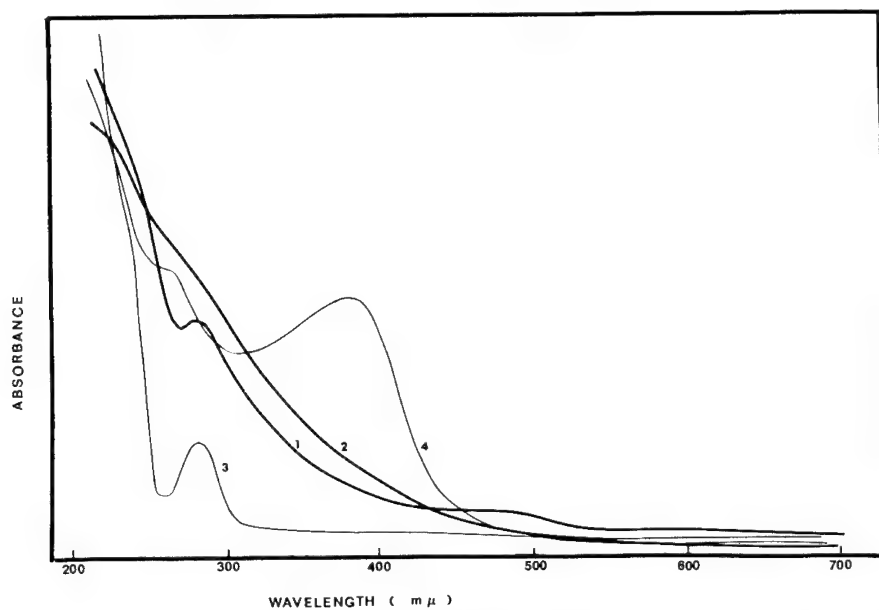
FIG. 3. Absorption spectra of (1) Polyphenol I, (2) Polyphenol II, (3) catechin, and (4) polycatechin in EtOH-dioxane-AlCl₃.
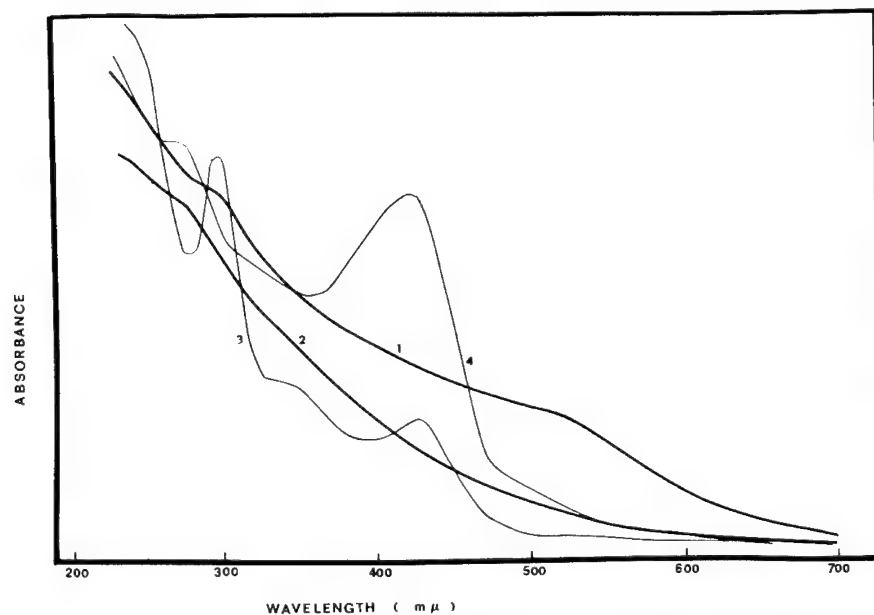
FIG. 4. Absorption spectra of (1) Polyphenol I, (2) Polyphenol II, (3) catechin, and (4) polycatechin in 0.1 N NaOH solution.

mic shift over the free acid form. This result had been found earlier for catechin, pyrocatechol, and for the phenolic acids from slash pine bark [1].

Polyphenol II, which was isolated in the presence of oxygen, had the same absorption shoulder at 260 mµ as polycatechin and general absorption in the visible

region. In contrast, polycatechin, obtained by dissolving catechin in 1% NaOH solution and stirring with oxygen, contained an absorption band at 260 mμ, but also contained a well-defined maximum at 390 mμ. A variety of mechanisms for the polymerization and oxidation of simple flavans has been suggested by Freudenberg [3], Hathway and Seakins [7] and Schulze and Flaig [20]. It is beyond the scope of this paper to discuss the various proposed mechanisms; however, it should be noted that products of these reactions contain two types of absorption spectra. Products from the oxidative polymerization of compounds which do not contain free phenolic groups at the 5 and 7 position, such as 3':4'-dihydroxyflavan and 5:7-di-o-methylcatechin exhibit phenolic absorption at 280 mμ, and general absorption at 300–600 mμ, while products formed from compounds containing phenolic hydroxyl groups at the 5 and 7 position, such as catechin and 5:7:3':4'-tetrahydroxyflavan, exhibit a well-defined maximum at 410–430 mμ, and two maxima at shorter wavelengths. Our study indicates that results with Polyphenol II are similar to the results obtained from simple 3':4' dihydroxyflavans. However, it should be kept in mind that the oxidative polymerization reaction done in these earlier studies were carried out under relatively mild conditions (pH 6 to 8), while our studies were done at much higher pH values.

Molecular Weight

The initial studies of the molecular weight were done directly on the alkaline extract using high-pressure liquid chromatography. Various types of packing materials (Bio-Beads, Styragel, Controlled Porosity Glass Beads) and a variety of solvent combinations were tried. However, none was satisfactory due to the strong molecular-associate tendency of the polyphenols. Consequently, it was necessary to convert the polyphenols into derivatives. Two types were used, namely a mixed methylated-acetylated derivative and the completely acetylated derivative.

The results obtained by high-pressure liquid chromatography and by vapor-phase osmometry are given in Table V. Polyphenol I had a molecular weight of 6,700 as determined by high-pressure gel permeation and 3,200 as determined by vapor-phase osmometry. Polyphenol II had a molecular weight of 1,700 by high-pressure gel permeation and 1,200 by vapor-phase osmometry. Apparently, during the extraction under oxygen, there was some depolymerization of the molecule.

Thermal Decomposition Properties

The thermal decomposition properties of the two alkaline-soluble fractions were initially characterized by using thermogravimetry (TG) and differential thermogravimetry (DTG) analyses (Fig. 5). The TG curves measure the weight loss versus temperature, while differential thermogravimetry is the rate of weight loss versus temperature. It was found by TG analyses that Polyphenol II gave 40% residue at 500°C, which is 8% less than Polyphenol I residue. The DTG curves showed that Polyphenol I decomposed at a maximum rate of 2%/min at 271°C, while Polyphenol II decomposed at the same maximum rate at 248°C. The thermal analysis curves of the two components were quite different from the other bark components such as holocellulose and lignin [21].

TABLE V
Molecular Weight Determination of the Polyphenol Derivatives

Compound	Analytical Method	Solvent Used	Molecular Weight
Polyphenol I[a]	High-pressure gel permeation	$CHCl_3$	6,700
Polyphenol I[b]	High-pressure gel permeation	$CHCl_3$	6,700
	Vapor-phase osmometry	$CHCl_3$	3,200
Polyphenol II[a]	High-pressure gel permeation	$CHCl_3$	1,700
Polyphenol II[b]	High-pressure gel permeation	$CHCl_3$	1,700
	Vapor-phase osmometry	DMF	1,200

[a] Methylated and acetylated polyphenol.
[b] Acetylated polyphenol.

TABLE VI
Products from the Pyrolysis of Polyphenols ($25°C-400°C$)

| Fraction | Composition[a] | |
	Polyphenol I	Polyphenol II
Amount pyrolyzed, grams	10.0	10.0
Noncondensable products, %	16.6	29.8
Condensable products, %	21.1	18.2
Fraction I	16.9	14.2
Fraction II	3.6	2.6
Fraction III	0.6	1.1
Residue, %	60.0	50.0

[a] Average taken from three pyrolysis runs.

TABLE VII

Nonphenolic Products from the Pyrolysis of Polyphenols I and II

Compound	Yield I	II	Identification Method
Water	14.76	13.52	a
Acetic acid	0.08	0.16	a,c
Methanol	0.01	0.02	a,c
Acetone	0.01	0.02	a,c
Benzene	0.01	0.02	a
Toluene	0.02	0.03	a
Oxalic acid	trace	0.88	b,d,e
Non-identified and polymerized material	0.42	0.94	

a Comparison of the retention time on gas chromatography.

b Comparison of the R_f values using TLC.

c Comparison of the thermal breaking patterns by vapor phase thermal fragmentation.

d Comparison of the retention time of the derivative on gas chromatography.

e Melting point.

Pyrolysis of the polyphenols was also conducted in a glass vessel under vacuum conditions (4 mm Hg). The temperature in the vessel was slowly heated for 4 hr to a maximum of 400°C and held at this temperature for 40 min. The resulting products were collected using an air condenser and two traps cooled to −30°C. The pyrolysis products collected in the traps were strongly acidic (Fraction I). The remaining material was washed with ether (Fraction II) and with methanol (Fraction III). The major products of pyrolysis were then identified by gas chromatography, thin layer chromatography and vapor-phase thermal fragmentation. The results are summarized in Tables VI–VIII. It was found that Polyphenol I on pyrolysis gave less noncondensable gases and more condensable products than Polyphenol II. The noncondensable materials consisted of mixtures of carbon monoxide and carbon dioxide. The aliphatic materials were found predominately in Fraction I. In general, more aliphatic products were found from pyrolysis of Polyphenol II than Polyphenol I. The major products were water, oxalic acid, and acetic acid (Table VI). Oxalic acid was mainly found in the methanol fraction of Polyphenol II.

Fraction II consisted largely of phenols. Our results showed that Polyphenol I gave 2.5 times more volatile phenols than Polyphenol II, with the main difference being in the amount of catechol, which was the major phenol found on pyrolysis of Polyphenol I (Table VIII).

The effect of temperature on pyrolysis was also studied by the method of pyrolytic gas chromatography to determine the distribution of low molecular weight phenol compounds versus temperature. Figure 6 shows the results of four major phenols generated during programmed pyrolysis at 200°C to 600°C with intervals

TABLE VIII
Phenols from the Pyrolysis of Polyphenols I and II

Phenolic Compound	Yield I	Yield II	Identification Method
Phenol	1.31	0.90	a,b,c
o-Cresol	0.10	0.19	a,b
m,p-Cresol	0.44	0.48	a,b,c
Guaiacol	0.67	0.30	a,b,c
2,6-Dimethylphenol	0.02	0.01	a,b
2,4-Dimethylphenol	0.02	0.04	a,b
3,5-Dimethylphenol	0.04	0.10	a,b,c
Creosol	0.11	0.08	a,c
Catechol	2.51	trace	a,b,c
4-Methylcatechol	0.18	trace	a,b,c
Resorcinol	0.03	trace	a,b,c
p-Hydroxybenzoic acid	0.18	trace	b

[a] Comparison of the retention time on gas chromatograph.
[b] Comparison of the R_f values using TLC.
[c] Comparison of the thermal-breaking patterns on vapor phase thermal fragmentation.

of 50°C. In the case of Polyphenol I, the yields of guaiacol and catechol were sharply increased from 200°C to 300°C and reached maxima at 400°C and 475°C, respectively. Beyond the maximum temperatures the yield of the two products decreased rapidly, with no guaiacol found above 500°C. In contrast, the maximum yields of phenol and m,p-cresols were obtained between 500°C and 600°C.

For Polyphenol II, guaiacol was the most prominent pyrolysis product at low temperature. Beyond 300°C, the amount of guaiacol slowly decreased, while the amount of phenol and m,p-cresols gradually increased. The maximum amounts of phenol and m,p-cresols were obtained around 500°C. Generally, these products showed a broad distribution versus temperature of pyrolysis. Since catechol and guaiacol are formed at relatively low temperatures, they are probably primary products from pyrolysis, while phenol and m,p-cresols are formed at relatively high temperatures and are probably secondary reaction products.

The distribution of pyrolysis products are related to the structure of the polyphenols. The major phenol product catechol found for Polyphenol I indicated that this type of structure must be an important part of Polyphenol I. However, the absence of phloroglucinol and small amounts of resorcinol found in the pyrolysis product suggests that the 1.3.5-trihydroxybenzene unit is either highly substituted or undergoes further degradation. The aliphatic products found in Fraction
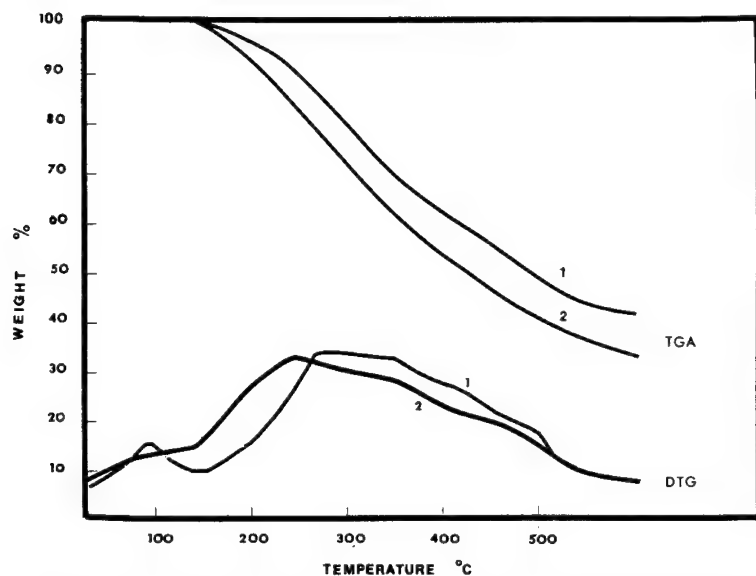
FIG. 5. Thermograms of the polyphenolic materials extracted under nitrogen (1) and oxygen (2).
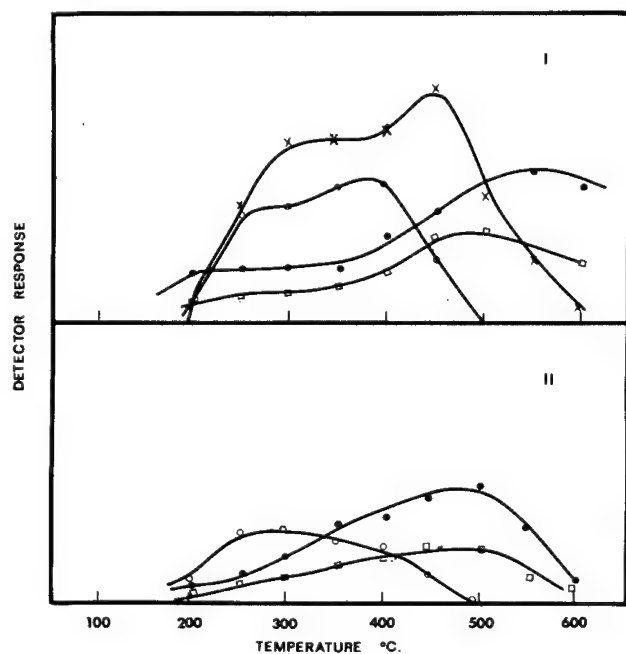

FIG. 6. Temperature effect on pyrolytic gas chromatography of polyphenols, (A) -●-●-●-●- Phenol (B) -O-O-O-O-O Guaiacol (C) -□-□-□-□-m,p-cresols (D) -x-x-x-x-x Catechol.

I could be formed from the unstable pyran ring proposed in the structure of polyphenolic acids. In Polyphenol II, only trace amounts of catechol could be detected by gas chromatography after pyrolysis, indicating that this catechol ring had been destroyed during extraction.

REFERENCES

[1] W. F. Erman and W. I. Lyness, *Tappi, 48,* 249 (1965).

[2] D. G. Roux and S. R. Evelyn, *Biochem. J., 70,* 344 (1958).

[3] K. Freudenberg, *J. Polymer Sci., 16,* 155 (1955).

[4] D. E. Hathway and J. W. T. Seakins, *Nature, 176,* 218 (1955).

[5] G. D. McGinnis and S. Parikh, *Wood Science, 7,* 295 (1975).

[6] R. W. Hemingway, *Tappi,* submitted for publication.

[7] D. E. Hathway and J. W. T. Seakins, *J. Chem. Soc.,* 1562 (1957). D. E. Hathway, ibid., 520 (1958).

[8] H. L. Hergert and E. F. Kurth, *J. Org. Chem., 18,* 521 (1953).

[9] K. D. Sears, R. L. Casebier, H. L. Hergert, G. H. Stout, and L. E. McCandlish, *J. Org. Chem., 39,* 3244 (1974).

[10] L. F. Hamilton and S. G. Simpson, *Quantitative Chemical Analysis,* 11th ed., Macmillan, New York, 1958, p. 168.

[11] E. J. Levy and D. G. Paul, *J. Gas Chromatog., 5,* 136 (1967).

[12] Y. P. Chang and R. L. Mitchell, *Tappi, 38,* 315 (1955).

[13] H. L. Hergert, L. E. Van Blaircom, J. C. Steinberg, and K. C. Gray, *Forest Prod. J., 15,* 485 (1965).

[14] E. F. Kurth and J. E. Smith, *Pulp Paper Mag. Can., 55,* 125 (1954).

[15] K. Freudenberg, *Angew. Chem., 27,* 1245 (1955).

[16] G. Gran and B. Althin, *Acta Chem. Scand. 4,* 967 (1950).

[17] T. Enkvist, B. Alm, and B. Holm, *Paperi ja Puu, 38,* 1 (1956).

[18] Q. P. Peniston and J. L. McCarthy, *J. Amer. Chem. Soc., 70,* 1329 (1948).

[19] K. Sarkanen and C. Schuerch, *Anal. Chem., 27,* 1245 (1955).

[20] H. Schulze and W. Flaig, *Annalen, 575,* 231 (1952).

[21] P. Fang, G. D. McGinnis, and E. J. Parish, *Wood and Fiber,* submitted for publication.

AUTHOR INDEX

Published Applied Polymer Symposia

1965   No. 1   High Speed Testing, Vol. V
                 Co-Chaired by A. G. H. Dietz and Frederick R. Eirich

1966   No. 2   Thermoanalysis of Fibers and Fiber-Forming Polymers
                 Edited by Robert F. Schwenker, Jr.
        No. 3   Structural Adhesives Bonding
                 Edited by Michael J. Bodnar

1967   No. 4   Weatherability of Plastic Materials
                 Edited by Musa R. Kamal
        No. 5   High Speed Testing, Vol. VI: The Rheology of Solids
                 Co-Chaired by Rodney D. Andrews, Jr., and Frederick R. Eirich
        No. 6   Fiber Spinning and Drawing
                 Edited by Myron J. Coplan

1968   No. 7   Polymer Modification of Rubbers and Plastics
                 Edited by Henno Keskkula

1969   No. 8   International Symposium on Polymer Modification
                 Edited by K. A. Boni and F. A. Sliemers
        No. 9   High Temperature Resistant Fibers from Organic Polymers
                 Edited by J. Preston
        No. 10   Analysis and Characterization of Coatings and Plastics
                 Edited by Claude A. Lucchesi
        No. 11   New Polymeric Materials
                 Edited by Paul F. Bruins
        No. 12   High Speed Testing, Vol. III: The Rheology of Solids
                 Co-Chaired by Rodney D. Andrews, Jr., and Frederick R. Eirich

1970   No. 13   Membranes from Cellulose and Cellulose Derivatives
                 Edited by Albin F. Turbak
        No. 14   Silicone Technology
                 Edited by Paul F. Bruins
        No. 15   Polyblends and Composites
                 Edited by Paul F. Bruins

1971   No. 16   Scanning Electron Microscopy of Polymers and Coatings
                 Edited by L. H. Princen
        No. 17   Mechanical Performance and Design in Polymers
                 Edited by O. Delatycki
        No. 18   Proceedings of the Fourth International
                 Wool Textile Research Conference
                 Edited by Ludwig Rebenfeld

1972   No. 19   Processing for Adhesives Bonded Structures
                 Edited by Michael J. Bodnar

1973   No. 20   United States—Japan Seminar on Polymer Processing and Rheology
                 Edited by D. C. Bogue, M. Yamamoto, and J. L. White
        No. 21   High-Temperature and Flame-Resistant Fibers
                 Edited by J. Preston and J. Economy
        No. 22   Polymeric Materials for unusual Service Conditions
                 Edited by Morton A. Golub and John A. Parker